

**Multi-Phased Remedial Investigation (RI)
of Surface and Subsurface Contamination of Soldier Creek
at Tinker AFB, Oklahoma
U.S. Air Force Installation Restoration Program**

FINAL

HEALTH AND SAFETY PLAN

MAY 1990

TINKER PROJECT NO: WWYK89-0196B
SITE ID NO: TINKER 0T03

Contract No.
DACA56-89-C-0062

WASTE SCIENCE AND TECHNOLOGY CORP.



SOLDIER CREEK RI/FS (NPL Site)

Prepared for: Tinker Air Force Base through
U.S. Army Corps of Engineers
Tulsa District

FINAL
HEALTH AND SAFETY PLAN
TINKER AFB - SOLDIER CREEK RI/FS

Prepared for:
TINKER AIR FORCE BASE
through
TULSA DISTRICT CORPS OF ENGINEERS
CONTRACT NO. DACA56-89-C-0062

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MAY 4, 1990

Prepared under:
INSTALLATION RESTORATION PROGRAM
TINKER PROJECT NO. WWYK89-0196B
SITE I.D. NO. TINKER OT03

TINKER AFB - SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN
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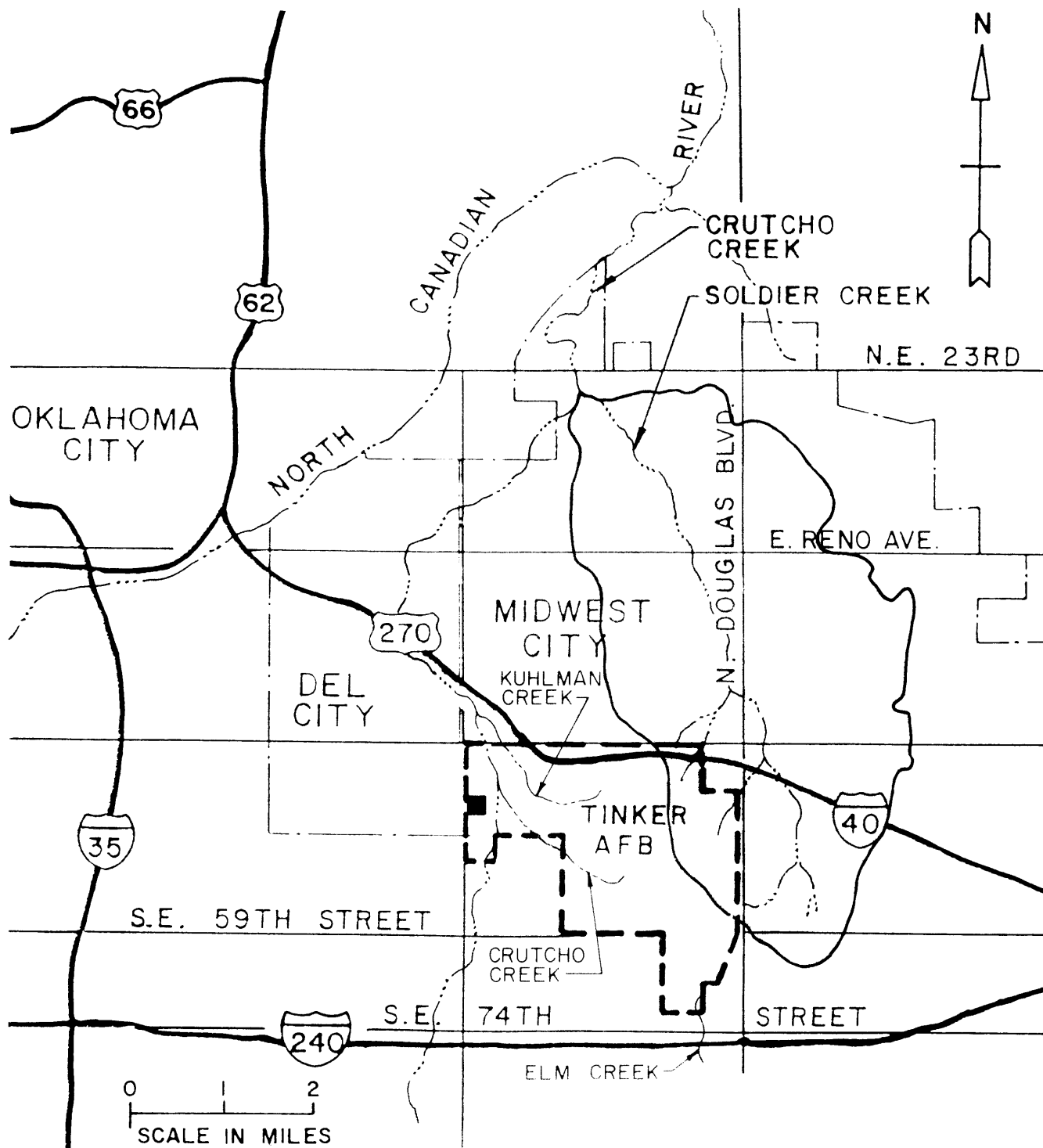


FIGURE 1
 SITE BOUNDARY - SOLDIER CREEK
 (APPROXIMATE DRAINAGE BOUNDARY)
 TINKER AFB - SOLDIER CREEK RI/FS
 HEALTH AND SAFETY PLAN

The Building 3001 site is comprised of the Building 3001 complex and two adjacent underground storage tank areas. The Building 3001 complex consists of an aircraft overhaul and modification complex to support the mission of the Oklahoma City Air Logistics Center. The primary activities at Building 3001 include disassembly, degreasing, cleaning, and inspection of aircraft and engine parts and components; plating, painting, heat treating, and testing of metal parts and components; assembly and repairing of accessories including electrical, valve and governor, gear box, tubing and cable, fuel controls, nozzles, pumps, and bearings; and assembly, testing, and packaging of aircraft and aircraft components. The tank areas contain active and abandoned underground storage tanks for fuel oil, diesel fuel, and gasoline, abandoned fuel and solvent tanks, and active solvent tanks. The IWTP receives industrial process discharge waters from the Building 3001 complex via a series of underground lines. Once received at the plant, these waters are treated and combined with treated sanitary wastewater prior to discharge to East Soldier Creek.

Table 1 lists the potential contaminants of concern for the Soldier Creek site. At this time, the following chemicals have been identified as the primary contaminants of concern at the site:

- o Cadmium
- o Chromium
- o Copper
- o Lead
- o 1,2-Dichlorobenzene
- o 1,4-Dichlorobenzene
- o Trans-1,2-Dichloroethene (t-1,2-DCE)
- o Tetrachloroethene (PCE)
- o Trichloroethene (TCE)
- o Cyanide

B. Status:

Active

C. Principal Disposal Method:

Industrial wastewaters are discharged to outfalls leading to Soldier Creek from the Industrial Wastewater Treatment Plant.

D. Features and Unusual Conditions:

Portions of site are located on private property.

TABLE 1

POTENTIAL CONTAMINANTS OF CONCERN
TINKER AFB – SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

<u>Inorganic Chemicals</u>	<u>CAS No.</u>	<u>Organic Chemicals (Continued)</u>	<u>CAS No.</u>
Arsenic	7440-38-2	1,4-Dichlorobenzene	106-46-7
Barium	7440-39-3	1,1-Dichloroethane	75-34-3
Cadmium	7440-43-9	1,2-Dichloroethane	107-06-2
Chromium	7440-41-7	1,1-Dichloroethene	75-35-4
Copper	7440-50-8	t-1,2-Dichloroethene	540-59-0
Cyanide	57-12-5	1,2-Dichloropropane	78-87-5
Iron	7435-89-6	cis-1,3-Dichloropropene	542-75-6
Lead	7435-52-1	Di-n-butyl Phthalate	84-74-2
Manganese	7439-96-5	Di-n-octyl Phthalate	117-84-0
Mercury	7439-97-6	Ethyl Benzene	100-41-4
Nickel	7440-02-0	Fluoranthene	206-44-0
Selenium	7782-49-2	Flourene	86-73-7
Silver	7440-22-4	Indeno(1,2,3-cd)pyrene	193-39-5
Zinc	7440-66-6	Methylene Chloride	75-09-2
		Naphthalene	91-20-3
		Pesticides	VARIOUS
		Phenanthrene	85-01-8
		Phenol	108-95-2
		Polychlorinated Biphenyls	VARIOUS
		Pyrene	129-00-0
		1,1,2,2-Tetrachloroethane	79-34-5
		Tetrachloroethene	127-18-4
		Toluene	108-88-3
		1,1,1-Trichloroethane	71-55-6
		1,1,2-Trichloroethane	79-00-5
		Trichloroethene	79-01-6
		Trichlorofluoromethane	75-69-4
		Vinyl Chloride	75-01-4
		Xylol (commercial grade xylene)	1330-20-7
<u>Organic Chemicals</u>	<u>CAS No.</u>		
Acenaphthylene	208-96-8		
Anthracene	120-12-7		
Benzene	71-43-2		
Benzo(a)anthracene	56-55-3		
Benzo(k)fluoranthene	207-08-9		
Benzo(g,h,i)perylene	191-24-2		
Benzo(a)pyrene	50-32-8		
Bis(2-ethylhexyl)phthalate	117-81-7		
Bromodichloromethane	75-27-4		
Bromoform	75-25-2		
Carbon Tetrachloride	56-23-2		
Chlorobenzene	108-90-7		
Chloroform	67-66-3		
2-Chloroethyl Vinyl Ether	110-75-8		
Chloromethane	74-87-3		
Chrysene	218-01-9		
Dibenzo(a,h)anthracene	53-70-3		
Dibromochloromethane	124-48-1		
1,2-Dichlorobenzene	95-50-1		
1,3-Dichlorobenzene	541-73-1		

E. History (worker or non-worker injury; complaints from public; previous Agency actions):

As part of the overall Air Force Installation Restoration Program (IRP), Tinker AFB began an investigation of previously used waste disposal sites in 1981. A basewide sampling program was conducted in 1983. Analytical results from the sampling program detected trichloroethene in the groundwater. Remedial investigations were conducted by the Tulsa COE from 1986-1989 to determine the nature and extent of groundwater contamination in the Building 3001 complex area. These investigations determined that chromium, in addition to trichloroethene, were contaminants of concern in the groundwater underlying Building 3001. On July 22, 1987, the Building 3001 site and the Soldier Creek site were added to the National Priorities List.

Investigation of possible sediment and surface water contamination of Soldier Creek began in 1984. Based on the results of sediment investigations completed in 1984 and 1985, a sediment removal action was performed on portions of East and West Soldier Creeks in early 1986. Visibly contaminated sediments were removed and disposed in a hazardous waste landfill. Post-removal sampling and visual inspection indicated that some contaminants may still be present in the sediments in Soldier Creek. A storm sewer investigation for Soldier Creek was completed in October 1989 to determine which storm sewers could potentially transmit contaminants from the Building 3001 complex area to Soldier Creek.

Building 3001 has undergone extensive investigations to determine the nature and extent of contamination at this site. A risk assessment and a feasibility study have also been completed for this site.

III. SCOPE OF WORK

A. Summary of Previous Site Activities.

Refer to Table 2.

B. Planned Site Activities and Dates.

Phase I Field Activities:

1. Sediment Sampling - Composite and grab sediment samples will be obtained from 42 sampling locations along Soldier Creek and its tributaries. Samples will be analyzed for VOCs, BNAs, metals, and cyanide as well as physical parameters.

TABLE 2

**SUMMARY OF PREVIOUS SITE ACTIVITIES
TINKER AFB – SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN**

Dates	Sampler	Sample Medium	Sample Analysis	Reference Document
6/84	Radian Corporation	Sediment	Metals, Fluoride, Cyanide, PCBs, Pesticides, Phenols, Nitrates, and Total Organic Carbon	Installation Restoration Program Phase II Confirmation/Quantification Stage 2 Final Report for Tinker AFB, Oklahoma
10/84	EPA	Sediment Water	Metals, VOAs, BNAs Metals, VOAs, BNAs, Water Quality Data	An Evaluation of the Effects of Wastewater Discharge from TAFB on Water Quality of Crutcho & Soldier Creeks
10/85	Harry Keith & Sons, Inc.	Sediment	Metals, VOAs, BNAs, PCBs, Pesticides Flouride, Nitrate, Cyanide, Phenols	Site Investigation Report
4/86&5/86	Harry Keith & Sons, Inc.	Sediment	Metals, BTX, VOCs	Sample Results – No Report
3/87–9/87	Tinker AFB	Water	VOCs	Sample Results – No Report IWTP & STP Discharges
6/87	Oklahoma State Department of Health	Sediment Water	Metals Metals, VOCs	Sample Results – No Report
9/86–7/87	Tinker AFB	Water	Water Quality Data(pH, TSS, Oil and Grease)	NPDES Analytical Results
Quarterly Sampling	Tulsa COE	Groundwater	VOCs, BNAs, Metals, TOC, pH Specific Conductivity, TICs	Tinker AFB Groundwater Assessment Building 3001 Remedial Investigations Building 3001 Supplemental Quarterly Remedial Investigations Groundwater Assessment Update Sample Results – No Report (3/88, 10/88)

TABLE 2 (Continued)

SUMMARY OF PREVIOUS SITE ACTIVITIES
TINKER AFB – SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

Dates	Sampler	Sample Medium	Sample Analysis	Reference Document
10/89	NUS Corporation	Water	VOCs, Metals(Cd, Cr, Cu, Pb, Ni, Zn) Oils and Grease, COD, Cyanide Total Phenols, Phosphorus, Chromium(Hex)	Final Storm Sewer Investigation for Soldier Creek

2. Surface Water Sampling - Composite and grab samples will be obtained at 42 sampling locations along Soldier Creek and its tributaries. Samples will be analyzed for VOCs, BNAs, metals, and cyanide as well as water quality parameters.
3. Off-base Groundwater Sampling - Groundwater samples will be obtained from four off-base private residential wells. Samples will be analyzed for VOCs, BNAs, metals (total and dissolved), and cyanide.
4. Surface Water Flow Measurement - Measurements of stream velocity and cross-sectional area will be made at each surface water sampling location and at 500 foot intervals along Soldier Creek from approximately East Reno Avenue to its headwaters just north of Southeast 59th Street.
5. Field Survey - A visual, walking survey of Soldier Creek and its tributaries emanating from Tinker AFB will be conducted to identify and measure all outfalls and storm drains which enter Soldier Creek. A field ground survey will be conducted to establish the stream bed profile at each 100 foot station and at each sampling location and to locate outfalls and storm drains.
6. RI-Derived Waste Disposal - This will include all activities to properly dispose of wastes generated during the Phase I field investigation.

Dates: April through June 1990.

C. Number of People on Site.

Potentially six to seven BVWST employees and subcontractor personnel throughout RI activities; at least two people at any one time.

D. Number of Days to Complete Work.

Forty-five to sixty calendar days for the Phase I Field Investigation.

IV. WASTE CHARACTERISTICS

A. Waste Type(s)

Liquid	_____	Solid	_____	Sludge	_____
Gas	_____	Other	<u>Contaminated groundwater, surface water, and sediment</u>		

B. Waste Characteristics

Corrosive	_____	Ignitable	_____	Radioactive	_____
Volatile	<u> X </u>	Toxic	<u> X </u>	Reactive	_____
Unknown	_____	Other (Name)	<u> Carcinogenic </u>		

V. HAZARD EVALUATION

A. Chemical Hazards

Respiratory Hazards:

- o Volatile organic compounds (including 1,4-dichlorobenzene; t-1,2-DCE; PCE; TCE).
- o Cadmium dust.
- o Chromium metal and insoluble salts.
- o Copper dust.

Dermal Hazards:

- o Volatile organic compounds (including 1,2-dichlorobenzene; 1,4-dichlorobenzene; t-1,2-DCE; TCE).
- o Soluble chromic and chromous salts.
- o Cyanides.

Table 3 presents physical characteristics and hazards associated with the identified contaminants of concern. Additional information (Occupational Health Guidelines) on selected chemicals can be found in Appendix B. Occupational Health Guidelines for the contaminants marked with an asterisk (*) are not available.

B. Physical Hazards

Slips, trips, and falls; poisonous snakes; quick muck; obstacles in creek; loose footing in creek; excessive algal growth on creek bottom.

TABLE 3
CONTAMINANTS OF CONCERN CHARACTERISTICS
AND HAZARDS
TINKER AFB - SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

CONTAMINANT OF CONCERN	CAS NO.	SYNONYM/ COMMERCIAL NAME	PHYSICAL DESCRIPTION	MOLECULAR WEIGHT	BOILING POINT (F)	INCOMPATIBILITIES	EXPOSURE LIMITS PEL**/TLV*** (mg/m ³)	TARGET ORGANS	HEALTH HAZARDS/CONTACT
*Arsenic	7440-38-2	Vary depending on specific compound	Appearance and odor vary for specific compound	Various	Various	Not Applicable	0.01/0.2 Potential carcinogen	Liver, kidneys, skin, lungs, lymphatic system	Dermal absorption; hyperemia pigmen- tation of skin
Barium	7440-39-3	Vary depending on specific compound	Appearance and odor vary for specific compound	Various	Various	Vary depending upon specific compound	0.5/0.5	Heart, CNS, skin, respiratory system, eyes	Skin burns, extra- systoles, hypo- kalemia
Cadmium dust (as Cd)	7440-43-8	Vary depending on specific compound	Appearance and odor vary for specific compound	Various	Various	Strong oxidizers, elemental sulfur, selenium, tellurium	0.2/0.05 Potential carcinogen	Respiratory system, kidneys, prostate, blood	Not Applicable
Chromium Metal/Insoluble Salts	7440-41-7	Vary depending on specific compound	Appearance and odor vary for specific compound	Various	Various	Strong oxidizers	1/0.5 Cr VI - carcinogenic	Respiratory system	Not Applicable
Soluble Chromium/Chromous Salts						Water	0.5/0.05	Skin	Dermal Sensitivity
Copper dust and mist (as Cu)	7440-50-8	Vary depending on specific compound	Odorless solid	Various	Various	Acetylene gas, magnesium metal	1/1	Respiratory system, skin, liver, kidneys	Eye irritant, dermatitis
Cyanides (as CN)	57-12-5	Potassium Cyanide/ Sodium Cyanide	White solid with a faint almond odor	65/49	-1300	Strong oxidizers	5/5	CVS, CNS, liver, kidneys, skin	Eye and skin irritant
Iron	7435-89-6	Vary depending on specific compound	Appearance and odor vary for specific compound	Various	Various	Calcium hypochlorite	10/5 (fume) -/1 (soluble)	Lungs	Not Applicable

TABLE 3 (Continued)
CONTAMINANTS OF CONCERN CHARACTERISTICS
AND HAZARDS
TINKER AFB - SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

CONTAMINANT OF CONCERN	CAS NO.	SYNONYM/ COMMERCIAL NAME	PHYSICAL DESCRIPTION	MOLECULAR WEIGHT	BOILING POINT (F)	INCOMPATIBILITIES	EXPOSURE LIMITS PEL**/TLV*** (mg/m ³)	TARGET ORGANS	HEALTH HAZARDS/CONTACT
*Lead, inorganic dust	7439-92-1	Vary depending on specific compound	Vary depending on specific compound	Various	Various	Strong oxidizers, hydrogen peroxide, active metals	0.05/0.15 Potential carcinogen	GI tract, CNS, kidneys, blood, gingival tissue	Not Applicable
Manganese	7439-96-5	Vary depending on specific compound	Gray solid	55	3808	Variable	5/5	Respiratory system, CNS, blood, kidneys	Not Applicable
Mercury and inorganic compounds (as Hg)	7439-97-9	Quicksilver	Silvery, mobile, odorless liquid	201	671	Acetylene, ammonia gases	0.1/0.05	Skin, respiratory system, CNS, eyes kidneys	Irritant to eyes and skin
Nickel, metal and soluble compounds (as Ni)	7440-02-0	Vary depending on specific compound	Vary depending on specific compound	Various	Various	Strong acids, sulfur, Ni(NO ₃) ₂ , wood	1/1 (metal), 0.1 (soluble)	Nasal cavities, lungs, skin	Pneumonia, potential carcino- gen
Selenium compounds (as Se)	7782-49-2	Vary depending on specific compound	Vary depending on specific compound	Various	Various	Acids, strong oxidizing agents	0.2/-	Upper respiratory, eyes, skin, liver, kidneys, blood	Dermatitis, blurry eyes
Silver metal and soluble compounds (as Ag)	7440-22-4	Vary depending on specific compound	Vary depending on specific compound	Various	Various	Acetylene, ammonia, hydrogen peroxide	0.01/0.1 (metal) -/0.01 (soluble)	Nasal septum, eyes, skin	Skin irritant, ulcerations
Zinc	7440-66-8	Vary depending on specific compound	Vary depending on specific compound	Various	Various	Flammable			
*Acenaphthylene	208-96-8	1,8-dihydroacenaphthalene, ethylenacenaphthalene	White needles	154.21	532				

TABLE 3 (Continued)
CONTAMINANTS OF CONCERN CHARACTERISTICS
AND HAZARDS
TINKER AFB - SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

CONTAMINANT OF CONCERN	CAS NO.	SYNONYM/ COMMERCIAL NAME	PHYSICAL DESCRIPTION	MOLECULAR WEIGHT	BOILING POINT (F)	INCOMPATIBILITIES	EXPOSURE LIMITS PEL**/TLV*** (mg/m ³)	TARGET ORGANS	HEALTH HAZARDS/CONTACT
*Anthracene	120-12-7		Yellow crystals with blue fluores- cence	178.22	844		Carcinogen		
Benzene	71-43-2	Benzol, Cyclohexatriene, Coal Tar Naphtha, Phenyl hydride	Colorless liquid with an aromatic odor	78	178	Strong oxidizers, chlorine, bromine with iron	0.01/0.01 Potential carcinogen	Blood, CNS, skin, bone marrow, eyes, respiratory system	Dermatitis
*Benzofluoranthracene	56-55-3								
*Benzofluoranthrene	207-08-9								
*Benzofluoranthrene	191-24-2								
*Benzofluoranthrene	50-32-8	3,4-Benzopyrene	Yellowish crystal	252.3	591		Carcinogen	Highly toxic	
*Benzofluoranthrene	117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	Liquid	390.54					
*Bromodichloromethane	75-27-4								
Bromoforn	75-25-2	Tri bromomethane	Colorless to yellow liquid with an odor like chloroform	253	298	Chemically active metals	5/5	Skin, liver, kidneys, respira- tory system, CNS	Skin irritant
Carbon Tetrachloride	56-23-2	Tetrachloromethane	Colorless liquid with ether-like odor	154	170	Chemically active metals	0.01/0.005 Potential carcinogen	CNS, liver, eyes, lungs, kidneys, skin	Skin irritant

TABLE 3 (Continued)
CONTAMINANTS OF CONCERN CHARACTERISTICS
AND HAZARDS
TINKER AFB - SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

CONTAMINANT OF CONCERN	CAS NO.	SYNONYM/ COMMERCIAL NAME	PHYSICAL DESCRIPTION	MOLECULAR WEIGHT	BOILING POINT (F)	INCOMPATIBILITIES	EXPOSURE LIMITS PEL*•TLV*** (mg/m ³)	TARGET ORGANS	HEALTH HAZARDS/CONTACT
Chlorobenzene	108-90-7	Monochlorobenzene, Chloro- benzol, Phenyl chloride, MCB	Colorless liquid with a mild aromatic odor	113	270	Strong oxidizers	0.075/0.075	Respiratory system, eyes, skin, CNS, liver	Skin and eye Irritant
Chloroform	67-66-3	Trichloromethane	Colorless liquid with pleasant, sweet odor	119	142	Strong caustics, chemically active metals	0.050 (cell)/0.01 Potential carcinogen	Liver, kidneys, heart, eyes, skin	Eye and skin Irritant
2-Chloroethyl Vinyl Ether	110-75-8	2-Chloroethoxy ethane	Colorless liquid	107	230				
*Chloromethane	74-87-3	Methyl Chloride	Colorless gas with a faint, sweet odor noticeable at dan- gerous concentra- tions	51	-12		0.10/0.05 Potential carcinogen	CNS, liver, kidneys, skin	Frostbite
*Chrysene	218-01-9	1,2-Benzphenanthrene	Crystals	228	838		Human carcinogen		
*Dibenz(a,h)anthracene	53-70-3	1,2,5,6-Dibenzanthracene		278			Human carcinogen		
*Dibromochloromethane	124-48-1	CHBr ₂ Cl	Clear, colorless, heavy liquid	209	241				Irritant
1,2-Dichlorobenzene	95-50-1	o-Dichlorobenzene, o-Dichlorobenzol	Colorless to pale yellow liquid with pleasant aromatic odor	147	358	Strong oxidizers, hot aluminum or aluminum alloys	0.05 (cell)/ 0.05 (cell)	Liver, kidneys, skin, eyes	Blister skin

TABLE 3 (Continued)
CONTAMINANTS OF CONCERN CHARACTERISTICS
AND HAZARDS
TINKER AFB - SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

CONTAMINANT OF CONCERN	CAS NO.	SYNONYM/ COMMERCIAL NAME	PHYSICAL DESCRIPTION	MOLECULAR WEIGHT	BOILING POINT (F)	INCOMPATIBILITIES	EXPOSURE LIMITS PEL*/TLV*** (mg/m ³)	TARGET ORGANS	HEALTH HAZARDS/CONTACT
*1,3-Dichlorobenzene	541-73-1	m-Dichlorobenzene	Colorless liquid	147	342	Combustible			
1,4-Dichlorobenzene	106-46-7	p-Dichlorobenzene, Dichloride, PDCB	Colorless solid with mothball-like odor	147	345	None hazardous	0.075/0.075	Liver, respiratory system, eyes, kidneys, skin	Jaundice, cirrhosis
1,1-Dichloroethane	75-34-3	Asymmetrical Dichloro- ethane, Ethylidene chloride, 1,1-Ethylidene dichloride	Colorless liquid with chloroform- like odor	99	135	Strong oxidizers and caustics	0.10/0.20	Skin, liver, kidneys	Skin Irritant
*1,2-Dichloroethane	107-06-2	Ethylene Dichloride, Glycol dichloride	Clear liquid with sweet odor like chloroform	99	183	Strong oxidizers and caustics, chemically active metals	0.05/0.01 Potential carcinogen	Kidneys, liver, eyes, skin, CNS	Dermatitis, eye Irritant
*1,1,2-Dichloroethane	540-59-0	1,2-Dichloroethylene, Acetylene dichloride, Dielom	Colorless liquid with ether-like, slightly acid odor, like chloro- form	97	113 to 140	Strong oxidizers	0.20/0.20	Respiratory system, eyes, CNS, skin	Skin contact toxic
1,2-Dichloropropane	78-87-5	Propylene Dichloride	Colorless liquid with odor like chloroform	113	205	Strong oxidizers and acids	0.075/0.075	Skin, eyes, res- piratory system, liver, kidneys	Skin Irritant
*cis-1,3-Dichloropropene	542-75-8	1,3-Dichloropropylene	Colorless liquid	111	219	Flammable	~0.001	Skin	Skin Irritant, toxic

TABLE 3 (Continued)
CONTAMINANTS OF CONCERN CHARACTERISTICS
AND HAZARDS
TINKER AFB - SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

CONTAMINANT OF CONCERN	CAS NO.	SYNONYM/ COMMERCIAL NAME	PHYSICAL DESCRIPTION	MOLECULAR WEIGHT	BOILING POINT (°F)	INCOMPATIBILITIES	EXPOSURE LIMITS PEL**TLV*** (mg/m³)	TARGET ORGANS	HEALTH HAZARDS/CONTACT
*Di-n-butylphthalate	84-74-2	n-Butyl Phthalate, Dibutyl Phthalate	Colorless, odorless, stable, oily liquid	278	644		-/5		Toxic
*Di-n-octylphthalate	117-84-0								
Ethyl Benzene	100-41-4	Phenylethane, Ethylbenzol	Colorless liquid with aromatic odor	106	277	Strong oxidizers	0.10/0.10	Eyes, upper respiratory system, skin, CNS	Eye and skin Irritant
*Fluoranthene	208-44-0	Idryl	Colored needles	202	482	Combustible			
*Fluorene	88-73-7	alpha-Diphenylenemethane, O-Biphenylenemethane	Small, white, crystalline solid	168	563	Combustible			
*Indeno(1,2,3-cd)pyrene	193-39-5								
Methylene Chloride	75-09-2	Dichloromethane, Methylene Dichloride	Colorless liquid with chloroform-like odor	85	104	Strong oxidizers and caustics, chemically active metals	0.50/0.05 Potential carcinogen	Skin, CVS, eyes, CNS	Eye and skin Irritant
Naphthalene	91-20-3	White tar, Naphthalin	Colorless to brown solid with odor of mothballs	128	190	Strong oxidizers	0.01/-	Respiratory system, eyes, skin	Eye and skin Irritant, derma- tosis
*Pesticides, Total	Various								
*Phenanthrene	85-01-8	None	Colorless, shining, crystalline solid	178	644				

TABLE 3 (Continued)

CONTAMINANTS OF CONCERN CHARACTERISTICS
AND HAZARDS
TINKER AFB - SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

CONTAMINANT OF CONCERN	CAS NO.	SYNONYM/ COMMERCIAL NAME	PHYSICAL DESCRIPTION	MOLECULAR WEIGHT	BOILING POINT (F)	INCOMPATIBILITIES	EXPOSURE LIMITS		HEALTH HAZARDS/CONTACT
							PEL**TLV***	TARGET ORGANS	
Phenol	108-95-2	Carbolic acid, Monohydroxy benzene	Colorless to pink solid or thick liquid with characteristic, sweet, tarry odor	94	359	Strong oxidizers, calcium hypochlorite	0.005/0.005	Liver, kidneys, skin	Burns skin, dermatitis
*Polychlorinated Biphenyls	Various								
*Pyrene	129-00-0	Benzodiphenanthrene	Colorless solid	204	759		Human carcinogen	Skin	Easily absorbed through skin
1,1,2,2-Tetrachloroethane	79-34-5	Symmetrical tetrachloroethane, Acetylene tetrachloride	Colorless to pale yellow liquid with sickly sweet odor like chloroform	168	285	Chemically active metals, strong caustics, hot metal in presence of steam	0.005/0.001 Potential carcinogen	Liver, kidneys, CNS	Dermatitis
Tetrachloroethene	127-18-4	Tetrachloroethylene, Perchloroethylene, Perk	Colorless liquid with odor like ether or chloroform	166	250	Strong oxidizers, chemically active metals	0.1/0.05 Potential carcinogen	Liver, kidneys, eyes, upper respiratory system, CNS	Eye and skin irritant
Toluene	108-88-3	Toluid, Phenyl Methane, Methyl Benzene	Colorless liquid with aromatic odor like benzene	92	231	Strong oxidizers	0.2/0.10	CNS, liver, skin, kidneys	Dermatitis
*1,1,1-Trichloroethane	71-55-6	Methyl Chloroform, Chloroethane	Colorless liquid	133	167		-10/35	Skin	Irritant to eyes and skin

TABLE 3 (Continued)
CONTAMINANTS OF CONCERN CHARACTERISTICS
AND HAZARDS
TINKER AFB - SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

CONTAMINANT OF CONCERN	CAS NO.	SYNONYM/ COMMERCIAL NAME	PHYSICAL DESCRIPTION	MOLECULAR WEIGHT	BOILING POINT (F)	INCOMPATIBILITIES	EXPOSURE LIMITS PEL**/TLV*** (mg/m ³)	TARGET ORGANS	HEALTH HAZARDS/CONTACT
1,1,2-Trichloroethane	79-00-5	Vinyl Trichloride, beta-Trichloroethane	Colorless liquid with sweet odor like chloroform	133	238	Strong oxidizers and caustics, chemically active metals	0.01/- Potential carcinogen	CNS, eyes, nose, liver, kidneys	Eye Irritant
*Trichloroethene	79-01-6	Trichloroethylene, Ethylene Trichloride, Triclene	Colorless liquid with sweet odor like chloroform	131	188	Strong caustics, chemically active metals	0.10/0.05 Potential carcinogen	Respiratory system, heart, liver, kidneys, CNS, skin	Eye Irritant, dermatitis
*Trichlorofluoromethane	75-69-4	Fluorotrichloromethane, Fluorocarbon-11	Colorless, nearly odorless, volatile liquid	138	75		-/1 (cell)		
*Vinyl Chloride	75-01-4	Chloroethylene, Chloroethene, Monochloroethylene, Vinyl C Monomer, Trividur, VC, VCM	Colorless gas, liquifies in freezing mixture	62.5	7	Copper oxidizing materials	0.001/0.005 Human carcinogen	Liver, CNS, blood, respiratory system, lymphatic system	
Xylof (commercial grade Xylene)	1330-20-7	Dimethylbenzene	Clear liquid with aromatic odor	106	Dependent upon grade	Flammable, strong oxidizers	0.1/0.1	CNS, eyes, GI tract, blood, liver, kidneys, skin	Eye Irritant, dermatitis

Notes:

* Occupational Health Guidelines for this contaminant are not available.

** Permissible exposure limit as found in 29 CFR 1910, Subpart Z, General Industry Standards for Toxic and Hazardous Substances, 8-hour Time-Weighted Average (TWA) unless otherwise noted.

*** Threshold Limit Value (TLV) recommended by the American Conference of Governmental Industrial Hygienists.

References:

HHS, 1985; Sax and Lewis, 1987; ACGIH, 1988; and Windholz, 1983.

C. Hazards Posed by Site Activities

Slips, trips, and falls associated with sampling, especially in the creek. Physical contact with contaminated groundwater, surface water, or sediment. Heat stress associated with field activities performed while wearing protective clothing.

D. Unusual Hazards

Potential for waders to fill with creek water during sampling. Some landowners may object to sampling teams on their property. Tinker AFB should obtain permission from landowners before sampling. Precautions should be taken to avoid vicious dogs that may be present in landowners' backyards.

E. Overall Hazard Level

Low to Moderate: Potential risk of contact with contaminated surface water greater since samplers must enter stream; waders are difficult to work in and potentially dangerous if they fill with water.

VI. PROCEDURES

A. Training Requirements

All personnel who will be engaged in hazardous waste operations must present, to the Site Safety Coordinator, certification of completion, within the 12 months prior to the beginning of site activities, of a hazardous waste site investigation training course or refresher course. The training must comply with OSHA regulations found at 29 CFR 1910.120 et. seq. The certification must be presented before site activities begin. Site specific safety training must be conducted for every person (workers and visitors) at the site before they are allowed onto the site.

B. Medical Monitoring Requirements

All personnel who will be engaged in hazardous waste operations must present to the Site Safety Coordinator certification of completion of a comprehensive medical monitoring examination within the 12 months prior to the beginning of site activities. The examination must comply with OSHA regulations found at 29 CFR 1910.120 et. seq. The certification must be signed by a medical doctor and indicate any work limitations placed on the individual. The certification also must specify that the individual is capable of working while wearing respiratory protective equipment. The certification must be presented before site activities begin.

C. Personnel Protective Equipment

Off-base Sampling and Survey Activities

Level of Protection: Modified Level D

Personnel Protective Equipment:
Cotton coveralls
Neoprene steel toe/shank boots
Disposable latex surgeon inner gloves
Nitrile rubber outer gloves

Additional Personnel Protective Equipment Based on Activity:
Any team member entering the stream bed will wear Saranex Tyvek coveralls and hip or chest waders. Lifelines will be used, and life preservers will be readily available.

Level of Protection: Level C

Additional Personnel Protective Equipment:
Fullface, air-purifying respirator with GMC-H Cartridges
or equivalent (changed at a minimum of every four hours).
Hooded Saranex Tyvek coveralls for team members entering stream bed.

Upgrade to Level C is to be based on the action levels listed below.

On-base Sampling and Survey Activities

Level of Protection: Modified Level D

Personnel Protective Equipment:
Tyvek coveralls
Neoprene steel toe/shank boots
Disposable latex surgeon inner gloves
Nitrile rubber outer gloves

Additional Modifications: Team members entering the stream bed will wear disposal latex butyl boot covers, or hip waders during on-base sampling and survey activities depending on creek conditions. Lifelines and life preservers will be used if stream depths warrant.

Level of Protection: Level C

Additional Personnel Protective Equipment:
Fullface, air-purifying respirator with GMC-H Cartridges
or equivalent (changed at a minimum of every four hours).
Hooded Tyvek coveralls.
Hooded Saranex Tyvek coveralls for team members entering stream bed.

Upgrade to Level C is to be based on the action levels listed below.

Action Levels

<u>Instrument</u>	<u>Reading</u>	<u>Action</u>
OVA or HNU (organic vapors)	Background	Level D
	Up to 5 ppm above background	Level C with appropriate cartridges.
	Greater than 5 ppm above background	Evacuate site. Take another reading in 15 minutes. If level persists contact BVWST Health and Safety Manager (HSM) and advise BVWST Project Manager (PM).
Radiation Meter	Background	Continue activities.
	Greater than background	Evacuate and advise BVWST PM.
Draeger Tube (CN)	Any indication	Evaluate site and consult BVWST HSM.
Draeger Tube (other species)	Species dependent	Consult BVWST HSM.

Monitoring Requirements

Ambient air monitoring will be conducted continuously while site activities are in progress. Monitoring instruments will include the following:

- o HNU (PID) or OVA (FID) for organic vapors.
- o Radiation detector.
- o Draeger pump and tubes for cyanide (other species as required).

The Site Safety Coordinator will take instrument readings every 15 minutes and record significant changes. The instrument readings will be recorded in a bound, permanent logbook maintained by the Site Safety Coordinator. Upgrade/downgrade decisions will be based on monitoring results in the breathing zone and the action levels listed above. Calibration and maintenance of monitoring equipment will be the responsibility of the Site Safety Coordinator and will be conducted in accordance with manufacturer's requirements as listed in the appropriate manual. Site workers are to be monitored for heat stress if working conditions warrant it and at the discretion of the Site Safety Coordinator.

D. Site Organization and Control

Map/Sketch Attached? Yes (Figure 1) Site Secured? No

Perimeter Identified? Yes (Figure 1)

Zone(s) of Contamination Identified? No - Verbal description provided.

An area of 5 to 30 feet on either side of the creek, depending on site conditions, will be the designated the Exclusion Zone. The corners will be staked, and the Site Safety Coordinator will define the boundaries with surveyor's tape prior to sampling. Exact zone boundaries will be selected at the discretion of the Site Safety Coordinator since surface details at the various sampling locations are likely to differ. A record of every person entering or exiting the site (workers and visitors) will be kept in a bound, permanent logbook maintained by the Site Safety Coordinator.

Entry into and exit from the Exclusion Zone for all personnel and equipment will be made through the Contamination Reduction Zone. Equipment and personnel washing facilities and a fire extinguisher will be provided in the Contamination Reduction Zone. The Site Safety Coordinator will be responsible for set up of the personnel and equipment washing facilities in the Contamination Reduction Zone. Personnel will make a final check of their protective equipment in the Contamination Reduction Zone before entering the Exclusion Zone. Personnel departing the Exclusion Zone will decontaminate their sampling equipment, monitoring equipment, and themselves before entering the Support Zone.

The Support Zone will include equipment staging and storage, break, and lunch areas. Emergency telephone numbers, directions to the hospital, and the Site Safety Plan will be posted in the Support Zone. A first aid kit will also be located in the Support Zone. An emergency vehicle will be parked just outside the Support Zone in the direction of the hospital.

All on-base sampling will be coordinated with the Tinker AFB Ground Safety Coordinator and safety briefings will be coordinated with the Tinker AFB Safety Office.

Sediment and surface water sampling will start at sampling locations downstream of Tinker AFB and move in an upstream direction to prevent cross contamination of samples.

E. Team Organization

<u>Team Member</u>	<u>Responsibility</u>
To Be Determined	Field Team Leader
To Be Determined	Site Safety Coordinator

F. Initial Procedures

- o Locate nearest available telephone.
- o Confirm and post emergency telephone numbers and route to hospital.
- o Designate at least one vehicle for emergency use.
- o Determine prevailing wind location, establish preliminary work zones (support area, contamination reduction area, exclusion area).
- o Perform initial site reconnaissance for RI.
- o Hold safety briefing for all participants before work begins. Safety meetings will be conducted at the minimum of once per week and documented for all workers.

G. Work Limitations

- o No eating, drinking, or smoking on-site.
- o No contact lenses to be worn on-site.
- o Work restricted to daylight hours only.
- o Buddy system in use at all times in exclusion zone.
- o BVWST personnel to wear TLD badges at all times when on or near the site.
- o Work to stop during thunderstorms or electrical storms.
- o No facial hair that would interfere with respirator fit.
- o Continuous air monitoring to occur while site activities are in progress.

H. Decontamination Procedures

For Personnel: Remove booties, dispose; remove outer gloves, dispose; remove APR; remove Tyvek coveralls, dispose; remove inner gloves, dispose; wash face and hands; remove boots. Sanitize APR or face piece after each daily use.

For Monitoring Equipment: Prevent monitoring equipment contamination by wrapping them or placing them in plastic bags or Visqueen. Dispose of plastic bags or Visqueen after use.

For Sampling Equipment: Equipment will be washed in a wash tub containing an Alconox solution and rinsed with deionized water over that tub. If oily materials are encountered during sampling, equipment will also be rinsed with a 95 percent ethyl alcohol solution, followed by a second deionized water rinse.

I. Disposal Procedures

Contaminated Liquids: Dispose in a 55-gallon DOT approved drum.

Contaminated Clothing: Dispose in a 55-gallon DOT approved drum.

J. Safety Equipment

- o Fire extinguisher - 10 lb. ABC type.
- o Eye-wash kits.
- o First aid kits meeting the provisions of 29 CFR 1926.50 (OSHA).
- o Blanket.

VII. EMERGENCY INFORMATION

A. Emergency Routes

The route to Midwest City Regional Hospital is dependent on which portion of the Soldier Creek site sampling activities are occurring. From the southern-most portion of the Soldier Creek site to Midwest City Regional Hospital: go to North Douglas Blvd.; continue north on North Douglas Blvd. until East Reno Ave.; turn left onto East Reno Ave. and continue west for approximately 2.4 miles; turn right onto Parklawn and continue north for approximately 0.4 miles; the hospital entrance is on the right.

The route to the Base Medical Facilities from Gate 20 or 21 is as follows: Enter Gate 20 or 21 from Douglas Boulevard and continue west for approximately 0.25 mile; turn right onto East Drive and continue north for approximately 1 mile; turn left onto Perimeter Drive and travel west for approximately 0.5 mile to "A" Avenue; turn left and continue south on "A" Avenue for approximately 0.25 mile until it curves west into 2nd Street; continue west on 2nd Street for approximately 1 mile; after passing Patrol Road, 2nd Street turns into Arnold Street; continue west on Arnold Street approximately 1 mile to the Base Medical Facilities. The route to the hospital from Gate 7 would be the same as from Gate 20 or 21 after entering Gate 7 and traveling south for less than 0.25 mile to Perimeter Drive and turning right.

The locations of the hospitals are shown on Figure 2.

The Site Safety Coordinator is to have an Oklahoma City map on-site at all times to locate the quickest, most direct route from the sampling team location to the hospitals, in case of an emergency.

B. Contingency Plan

1. Pre-Emergency Planning

The Field Team Leader or Site Safety Coordinator will contact the local hospital emergency room, poison control center, police department, fire department, ambulance, and other emergency services before field activities begin. The Field Team Leader or Site Safety Coordinator will inform the hospital emergency room and ambulance service of probable emergencies and fill out insurance information at the hospital prior to the start of the RI. This will assist local personnel in being prepared should an emergency arise during the investigation.

Before the investigation begins, the Site Safety Coordinator will hold a site briefing. All members of the investigation team will attend this meeting. During this meeting, the Site Safety Coordinator will discuss personnel safety equipment use, maintenance, and limitations; accident prevention procedures; accident response procedures; accident reporting procedures; and decontamination procedures. Questions about the project will be answered and the Health and Safety Plan Certification will be signed by all team members during the initial briefing. The Site Safety Coordinator will also hold a similar meeting with individuals who later become a part of the investigation team before they take part in investigation activities. Subsequent periodic briefings will be held at a minimum of once per week throughout the course of the investigation. Unsafe practices

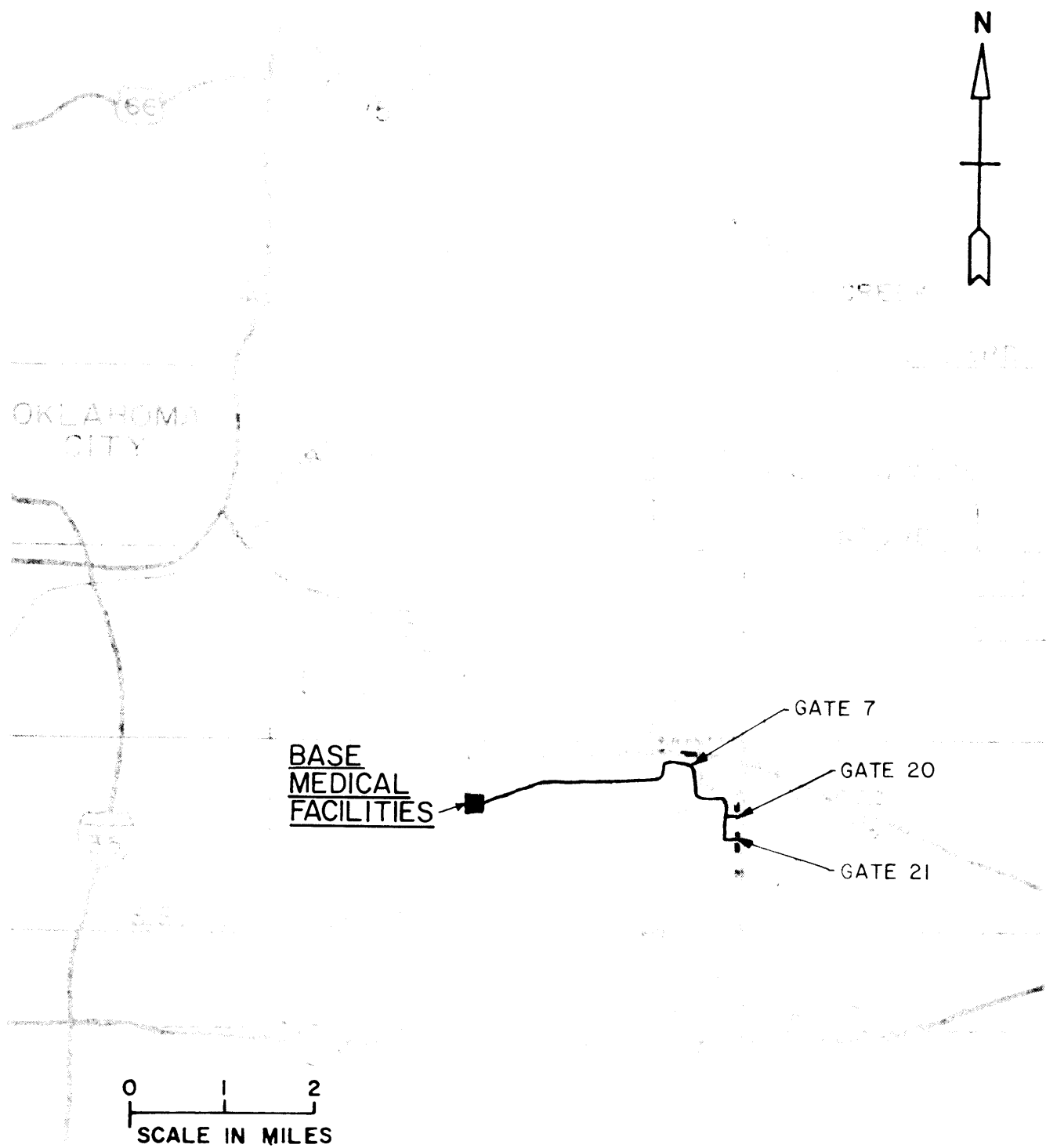


FIGURE 2
HOSPITAL LOCATIONS
TINKER AFB - SOLDIER CREEK RI/FS
HEALTH AND SAFETY PLAN

which are noted during the investigation, changes in site conditions which require modification of the Health and Safety Plan or other safety issues will be discussed during these briefings.

2. Personnel Roles, Lines of Authority, Training and Communication

The Site Safety Coordinator will be responsible for all decisions relating to site safety. This will include overseeing air and cold stress monitoring, as well as establishing appropriate levels of personnel protection and work schedules for the investigation. The Site Safety Coordinator will ensure that all participants conduct their work in accordance with the Health and Safety Plan and applicable safety rules, and will direct any assigned employee to leave the site if the employee fails to observe safety requirements or in any way creates a safety hazard.

3. Emergency Prevention and Recognition

Emergency prevention and recognition measures include air monitoring activities, cold stress monitoring, and recognition of hazards by the team members, and cold stress monitoring are discussed in Section VI.

All employees will be directed to avoid contact with contaminated substances. This will include avoiding walking through pools, puddles, mud, etc., and avoiding kneeling or sitting on the ground, or leaning or sitting on drums or equipment.

All employees will be directed to bring to the attention of the Site Safety Coordinator and Field Team Leader any unsafe condition, practice, or circumstance associated with or resulting from the remedial investigation.

4. Safe Distances and Places of Refuge

The storage tanks represent an unusual hazard at the Kem-Pest site. The proposed contamination reduction and support areas will be located approximately 135 feet upwind from the storage tanks, in order to provide a safe distance and place of refuge.

5. Site Organization and Control

Site organization and control are discussed in Section VI.D.

6. Evacuation Routes

The preferred evacuation route is via the Tinker AFB gates shown on Figure 2. The emergency route to the hospital will be posted in the Support Area and taped to the dashboard of the emergency vehicle.

7. Decontamination

Decontamination procedures are specified in Section VI.H. In the event of an emergency, limited personnel decontamination will be conducted, if possible, but not if time is critical in obtaining medical assistance.

8. Emergency Medical Treatment and First Aid

All team members will have been trained as specified in Section VI.A. At least two members of the team will be certified in CPR and First Aid.

9. Emergency Alerting and Response Procedures

In cases of immediate hazard to employees or the public, employees on the scene will take all practicable steps to eliminate, neutralize, or avoid the hazard. This may include leaving the site. Follow-up consultation with the Field Team Leader, Site Safety Coordinator, and BVWST Health and Safety Manager will be made at the first opportunity. In such circumstances, the Field Team Leader will take the steps necessary to ensure that the investigation is completed safely. These steps may include changes in field procedures, removal or neutralization of a hazard, consultation with appropriate experts, or use of specialists. All such actions will be coordinated with and approved by the BVWST Health and Safety Manager.

In cases where the hazard is not immediate, the employee will consult the BVWST Health and Safety Manager regarding appropriate corrective measures.

In the event that any member of the party experiences any adverse effects or symptoms of exposure while on-site, the entire party will immediately leave the site and seek appropriate medical aid. Those on-site will evacuate the site through the access gate west of the building. The Site Safety Coordinator will be in charge of health and safety measures. If he is not present or is injured, the Field Team Leader will be in charge.

In the event that any member of the party is overcome, incapacitated, or traumatically injured while on-site, the remaining members will immediately don appropriate protective equipment (at least one level above the level of personnel protection of the victim) and make reasonable efforts to rescue the affected person.

Once removed from the site, the affected person will not be left unattended, and medical assistance will be summoned. If it is necessary to drive the victim to the hospital, two field personnel will accompany the victim. One other person from the field crew will be designated by the Site Safety Coordinator to call ahead to the emergency room and to provide information on the accident before the victim arrives. If the Site Safety Coordinator is injured, the Field Team Leader will call ahead to the hospital.

When it is determined that the problem was due to chemical exposure, all members of the party exposed to those chemicals will proceed expeditiously, in a group, to the hospital. In those cases where personal contamination has occurred, all persons involved will make every reasonable effort to decontaminate themselves to minimize spreading of contaminants.

a. Procedures for Emergencies Posing An Immediate Threat to Life, Limb, or Health of One or More Personnel in the Exclusion Area

Examples: explosion, excessive smoke, fire, excessive concentrations of organic contaminants, equipment accident, person unconscious, nausea, dizziness, safety or protective equipment malfunction.

- 1) Person involved in or witnessing accident or other threatening situation will activate his personal alarm horn immediately.
- 2) Injured persons' partners or other personnel close to them will lend assistance. Personnel will not unduly jeopardize their own lives to assist an injured person. The injured person will be moved only when necessary to avoid further hazards.
- 3) All activity in the Exclusion Area will cease and personnel not involved in providing assistance to injured or endangered personnel will depart to the Support Area.
- 4) The Site Safety Coordinator will immediately call the proper authorities (ambulance, fire, police, poison control center, rescue teams, etc.). If the Site Safety Coordinator is injured or absent, the Field Team Leader will call the proper authorities.
- 5) Personnel will not reenter the Exclusion Area until allowed by the Field Team Leader. The Field Team Leader will assess the nature of the emergency and correct the matter before allowing reentry.
- 6) A complete written report of the incident will be made by the injured personnel and the Field Team Leader.

b. Procedures for Minor Accidents in the Exclusion Area

Examples: sprains, small cuts or scrapes, equipment malfunction.

- 1) Person involved will initiate the appropriate corrective procedures.
- 2) Person injured will cease his work, notify partner, and exit with the partner to the Contamination Reduction Area and obtain adequate medical attention.

c. Procedures for Emergencies Posing an Immediate Threat to Life, Limb, or Health of One or More Personnel in the Contamination Reduction or Support Area

- 1) Persons at the scene will lend assistance and perform the necessary first aid, CPR, etc.
- 2) The Site Safety Coordinator will immediately call the proper authorities (ambulance, fire, police, poison control center, rescue teams, etc.). If the Site Safety Coordinator is injured or absent, the Field Team Leader will call the proper authorities.
- 3) Personnel in the Exclusion Area will be signaled to depart the site if they could be affected by the accident.
- 4) A complete written report of the incident will be made by the injured personnel and the Field Team Leader.

d. Procedures for Minor Accidents in the Contamination Reduction or Support Area

The person involved will initiate the appropriate corrective measures and obtain adequate medical attention.

10. Follow-up

In order to comply with federal and state laws concerning workers' compensation and insurance coverage, all accidents will be reported immediately to the BVWST Workers' Compensation Administrator, Diane S. Mettenbrink (913/339-8561). The BVWST Health and Safety Manager will be notified immediately so that corrective actions can be implemented. In addition, the EPA RPM will be notified. If immediate notification is not possible, the accident will be reported within 24 hours of occurrence.

Injuries and property damage will be reported to the Tinker AFB Safety Office as soon as possible after the occurrence.

An injury or accident report form will also be completed and sent to the BVWST Controller, G.F. Cockrell (A-1, Kansas City).

11. PPE and Emergency Equipment

PPE and emergency equipment are specified in Sections VI.C. and VI.J.

C. Emergency Contacts (BVWST)

1. Raul E. Filardi/Assistant Project Manager
Phone: 913/339-8816 (w)
913/888-5792 (h)
2. Dr. George A. Carson/BVWST Health and Safety Manager
Phone: 913/339-8847 (w)
913/782-7688 (h)
3. Dr. Eugene Welter, MD/Business & Industry Health Group
Phone: 913/894-6600 (w)
4. Diane S. Mettenbrink/Workman's Compensation Administrator
Phone: 913/339-3313 (w)

D. Local Emergency Contacts

1. Fire (405) 739-1341 or 911
2. Police (405) 739-1300 or 911
3. Ambulance (405) 733-1414 or 911
4. Hospital (405) 737-4411 (Midwest City Regional Hospital)

VIII. PLAN PREPARATION

PREPARED BY:	<u>B.L. Anderson</u>	Date:	<u>11/13/89</u>
REVISED BY:	<u>B.L. Anderson</u>	Date:	<u>02/20/90</u>
REVIEWED BY:	<u>(Project Manager)</u>	Date:	<u></u>
APPROVED BY:	<u>(BVWST HSM)</u>	Date:	<u></u>

NOTICE

This health and safety plan is produced for the use of BVWST on the specific Project indicated herein. This safety plan is not intended or represented to be suitable for use by others on the Project, or for reuse on extensions of the Project, or for use on any other project. Any use without written verification or adaptation by BVWST will be at the user's sole risk and without liability or legal exposure to BVWST.

IX. PLAN DISTRIBUTION

Suzette Turner/Tulsa COE
Vernon M. Reid/BVWST
Raul E. Filardi/BVWST
Janet S. Walstrom/BVWST

George A. Carson/BVWST
Site Safety Coordinator(s)/BVWST
All On-site Personnel
Central Project File

X. CERTIFICATIONS

(Note: This page should be retained by the Site Safety Coordinator and incorporated into the project file.)

By my signature, I certify that:

1. I have read,
2. I understand, and
3. I will abide by

the Health and Safety Plan for the Tinker AFB - Soldier Creek site.

<u>Printed Name</u>	<u>Signature</u>	<u>Date</u>	<u>Affiliation</u>
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APPENDIX A

REPORT OF HAZARDOUS WASTE SITE INVESTIGATION
PERSONNEL ACTIVITIES

APPENDIX A

REPORT OF HAZARDOUS WASTE SITE INVESTIGATION
PERSONNEL ACTIVITIES

B&V WASTE SCIENCE AND TECHNOLOGY CORP.

REPORT OF HAZARDOUS WASTE SITE INVESTIGATION PERSONNEL ACTIVITY

SITE NAME: Tinker AFB - Soldier Creek
PROJECT NUMBER: 40054
SITE SAFETY COORDINATOR: To Be Announced
DATES ON SITE: _____

SITE ACTIVITY: Sediment Sampling, Surface Water Sampling, Off-base Groundwater Sampling, Surface Water Flow Measurement, Field Survey

Employee Name	Total Days		Days at the Site in				Number of days as SSC		Activities	
	Onsite	Offsite	Level B	Level C	Level D	or	Level B	Level C	Level D	While Onsite
1.										
2.										
3.										
4.										
5.										
6.										

BRIEF SUMMARY OF SITE SAFETY ACTIVITIES (ADEQUACY OF SSP, UPGRADE/DOWNGRADE DECISIONS, OTHER PROBLEMS ENCOUNTERED, SUGGESTIONS FOR FUTURE WORK, ETC.):

Signed _____ Date _____
Site Safety Coordinator

B&V WASTE SCIENCE AND TECHNOLOGY CORP.

REPORT OF HAZARDOUS WASTE SITE INVESTIGATION PERSONNEL ACTIVITY

SITE NAME: Tinker AFB - Soldier Creek
PROJECT NUMBER: 40054
SITE SAFETY COORDINATOR: To Be Announced
DATES ON SITE: _____

SITE ACTIVITY: Sediment Sampling, Surface Water
Sampling, Off-base Groundwater Sampling, Surface
Water Flow Measurement, Field Survey

Employee Name	Total Days		Days at the Site in			Number of days as SSC		Activities	
	Onsite	Offsite	Level B	Level C	Level D	Level B	Level C	Employees Performed	While Onsite
1.									
2.									
3.									
4.									
5.									
6.									

BRIEF SUMMARY OF SITE SAFETY ACTIVITIES (ADEQUACY OF SSP, UPGRADE/DOWNGRADE DECISIONS, OTHER PROBLEMS ENCOUNTERED, SUGGESTIONS FOR FUTURE WORK, ETC.):

Signed _____ Date _____
Site Safety Coordinator

APPENDIX B

OCCUPATIONAL HEALTH GUIDELINES FOR
SELECTED POTENTIAL CONTAMINANTS OF
CONCERN

APPENDIX B

OCCUPATIONAL HEALTH GUIDELINES FOR
SELECTED POTENTIAL CONTAMINANTS OF
CONCERN

Occupational Health Guidelines (HHS, 1978) are provided in this appendix for the following selected contaminants of concern:

Inorganic Chemicals

- Soluble Barium compounds (as Barium)
- Cadmium Dust (as Cadmium)
- Cadmium Fume
- Chromium Metal and Insoluble Chromium Salts
- Soluble Chromic and Chromous Salts (as Chromium)
- Copper Dusts and Mists
- Copper Fume
- Cyanide
- Iron Oxide Fume
- Manganese
- Inorganic Mercury
- Nickel Metal and Soluble Nickel Compounds
- Selenium and Its Inorganic Compounds (as Selenium)
- Silver Metal and Soluble Silver Compounds
- Zinc Oxide Fume

Organic Chemicals

- Benzene
- Bromoform
- Carbon Tetrachloride
- Chlorobenzene
- Chloroform
- o-Dichlorobenzene
- p-Dichlorobenzene
- 1,1-Dichloroethane
- 1,2-Dichloroethylene
- Propylene Dichloride
- Ethyl Benzene
- Methylene Chloride
- Napthalene
- Phenol
- 1,1,2,2-Tetrachloroethane
- Tetrachloroethylene
- Toluene
- 1,1,2-Trichloroethane

Occupational Health Guidelines (HHS, 1978) are provided in this appendix for the following selected contaminants of concern:

Inorganic Chemicals

Soluble Barium compounds (as Barium)
Cadmium Dust (as Cadmium)
Cadmium Fume
Chromium Metal and Insoluble Chromium Salts
Soluble Chromic and Chromous Salts (as Chromium)
Copper Dusts and Mists
Copper Fume
Cyanide
Iron Oxide Fume
Manganese
Inorganic Mercury
Nickel Metal and Soluble Nickel Compounds
Selenium and Its Inorganic Compounds (as Selenium)
Silver Metal and Soluble Silver Compounds
Zinc Oxide Fume

Organic Chemicals

Benzene
Bromoform
Carbon Tetrachloride
Chlorobenzene
Chloroform
o-Dichlorobenzene
p-Dichlorobenzene
1,1-Dichloroethane
1,2-Dichloroethylene
Propylene Dichloride
Ethyl Benzene
Methylene Chloride
Naphthalene
Phenol
1,1,2,2-Tetrachloroethane
Tetrachloroethylene
Toluene
1,1,2-Trichloroethane

Occupational Health Guideline for Soluble Barium Compounds (as Barium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble barium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Barium nitrate

- Formula: $\text{Ba}(\text{NO}_3)_2$
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium oxide

- Formula: BaO
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium carbonate

- Formula: BaCO_3
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium chloride

- Formula: BaCl_2
- Synonyms: None
- Appearance and odor: Odorless white solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble barium compounds is 0.5 milligram of soluble barium compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

• Routes of exposure

Soluble barium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

• Effects of overexposure

1. *Short-term Exposure:* Soluble barium compounds may cause local irritation of the eyes, nose, throat, bronchial tubes, and skin. Soluble barium compounds may also cause severe stomach pains, slow pulse rate, irregular heart beat, ringing of the ears, dizziness, convulsions, and muscle spasms. Death may occur.

2. *Long-term Exposure:* None known

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble barium compounds.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to soluble barium compounds at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the heart, lungs, and nervous system should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Soluble barium compounds cause human lung damage. Surveillance of the lungs is indicated.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Occupational Health Guideline for Soluble Barium Compounds (as Barium)

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble barium compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Barium nitrate

- Formula: $\text{Ba}(\text{NO}_3)_2$
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium oxide

- Formula: BaO
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium carbonate

- Formula: BaCO_3
- Synonyms: None
- Appearance and odor: Odorless white solid.

Barium chloride

- Formula: BaCl_2
- Synonyms: None
- Appearance and odor: Odorless white solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble barium compounds is 0.5 milligram of soluble barium compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

• Routes of exposure

Soluble barium compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

• Effects of overexposure

1. *Short-term Exposure:* Soluble barium compounds may cause local irritation of the eyes, nose, throat, bronchial tubes, and skin. Soluble barium compounds may also cause severe stomach pains, slow pulse rate, irregular heart beat, ringing of the ears, dizziness, convulsions, and muscle spasms. Death may occur.

2. *Long-term Exposure:* None known

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble barium compounds.

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The following medical procedures should be made available to each employee who is exposed to soluble barium compounds at potentially hazardous levels:

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—FVC and FEV (1 sec): Soluble barium compounds are respiratory irritants. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Electrocardiogram: Barium compounds may cause cardiac arrhythmias and may have a direct effect on the cardiac muscle. Periodic surveillance of the heart is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

• **Summary of toxicology**

Soluble barium salts cause severe gastroenteritis and systemic effects by ingestion. Intravenous injection of barium compounds in animals causes a strong, prolonged stimulation of muscle resulting in hyperperistalsis, bladder contraction, vasoconstriction, and irregular contraction of the heart followed by arrest in systole. Animals also exhibit stimulation of the central nervous system followed by paralysis. Ingestion of barium carbonate by humans causes gastroenteritis, muscular paralysis, slow pulse rate, extrasystoles, and hypokalemia. Heavy industrial exposure to dusts of barium sulfate or barium oxides may produce a benign pneumoconiosis, termed baritosis. It results in no impairment of ventilatory function, although signs of mild bronchial irritation may occur. Characteristic x-ray changes are those of small, dense, circumscribed nodules evenly distributed throughout the lung fields, reflecting the radio-opacity of the barium dust. Bronchial irritation has been reported from the inhalation of barium carbonate dust. Barium hydroxide and barium oxide are strongly alkaline in aqueous solution, causing severe burns of the eye and irritation of the skin.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Barium nitrate**

1. Molecular weight: 261.4
2. Boiling point (760 mm Hg): Greater than 592 C (greater than 1098 F) (decomposes)
3. Specific gravity (water = 1): 3.24
4. Vapor density (air = 1 at boiling point of barium nitrate): Not applicable
5. Melting point: 592 C (1098 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 9.2
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium oxide**

1. Molecular weight: 153.3
2. Boiling point (760 mm Hg): 2000 C (3632 F)
3. Specific gravity (water = 1): 5.72
4. Vapor density (air = 1 at boiling point of barium oxide): Not applicable
5. Melting point: 1921 C (3490 F)

6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium carbonate**

1. Molecular weight: 197.3
2. Boiling point (760 mm Hg): 1300 C (2372 F) (decomposes)
3. Specific gravity (water = 1): 4.25
4. Vapor density (air = 1 at boiling point of barium carbonate): Not applicable
5. Melting point: Decomposes at 1300 C (2372 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0022
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium chloride**

1. Molecular weight: 208.3
2. Boiling point (760 mm Hg): 1560 C (2840 F)
3. Specific gravity (water = 1): 3.86
4. Vapor density (air = 1 at boiling point of barium chloride): Not applicable
5. Melting point: 963 C (1765 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 36
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: For barium nitrate, elevated temperatures may cause melting and decomposition; for the other compounds, none hazardous.
2. Incompatibilities: Contact of barium oxide with water, carbon dioxide, or hydrogen sulfide may cause fires and explosions. Contact of barium carbonate with acids causes formation of carbon dioxide gas that may cause suffocation in enclosed spaces. Contact of barium nitrate with organic matter and combustible materials may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen and carbon monoxide) may be released in a fire involving barium nitrate.

4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: For barium nitrate, data not available; for the other compounds, not applicable.
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Large amounts of water should be used on adjacent fires.

• **Warning properties**

According to Grant, barium chloride causes "considerable iritis, which subsides in a few days" when "tested

—FVC and FEV (1 sec): Soluble barium compounds are respiratory irritants. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Electrocardiogram: Barium compounds may cause cardiac arrhythmias and may have a direct effect on the cardiac muscle. Periodic surveillance of the heart is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

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8. Evaporation rate (butyl acetate = 1): Not applicable

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2. Boiling point (760 mm Hg): 2000 C (3632 F)
3. Specific gravity (water = 1): 5.72
4. Vapor density (air = 1 at boiling point of barium oxide): Not applicable
5. Melting point: 1921 C (3490 F)

6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Reacts

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium carbonate**

1. Molecular weight: 197.3
2. Boiling point (760 mm Hg): 1300 C (2372 F) (decomposes)
3. Specific gravity (water = 1): 4.25
4. Vapor density (air = 1 at boiling point of barium carbonate): Not applicable
5. Melting point: Decomposes at 1300 C (2372 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0022
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Barium chloride**

1. Molecular weight: 208.3
2. Boiling point (760 mm Hg): 1560 C (2840 F)
3. Specific gravity (water = 1): 3.86
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4. Special precautions: None

• **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: For barium nitrate, data not available; for the other compounds, not applicable.
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: Large amounts of water should be used on adjacent fires.

• **Warning properties**

According to Grant, barium chloride causes "considerable iritis, which subsides in a few days" when "tested

in neutral 0.08 to 0.1 M solution on rabbit eyes by injection into the cornea or by dropping for 10 minutes on the eye after the corneal epithelium was removed to facilitate penetration." Grant states that "both the oxide and hydroxide are capable of causing severe alkali burns of the eye, similar to those produced by calcium hydroxide."

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection on a cellulose membrane filter followed by leaching in hot water, solution of sample in acid, and analysis in an atomic absorption spectrophotometer. An analytical method for soluble barium compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing

necessary to prevent repeated or prolonged skin contact with barium carbonate, barium chloride, barium nitrate, or liquids containing these compounds.

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with barium oxide or liquids containing barium oxide, where skin contact may occur.

• If employees' clothing has had any possibility of being contaminated with barium carbonate, barium chloride, barium nitrate, barium oxide, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.

• Clothing contaminated with barium carbonate, barium chloride, barium nitrate, or barium oxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.

• Where exposure of an employee's body to barium oxide or liquids containing barium oxide may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with barium carbonate, barium chloride, barium nitrate, or barium oxide should be removed promptly and not reworn until the contaminant is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of barium oxide or liquids containing barium oxide contacting the eyes.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where barium carbonate, barium chloride, barium nitrate, or liquids containing these compounds may contact the eyes.

• Where there is any possibility that employees' eyes may be exposed to barium oxide or liquids containing barium oxide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Workers subject to skin contact with barium oxide or liquids containing barium oxide should wash any areas of the body which may have contacted barium oxide at the end of each work day.

• Skin that becomes contaminated with barium carbonate, barium chloride, or barium nitrate should be promptly washed or showered to remove any contaminant. In the case of barium carbonate, employees should use soap or mild detergent and water for washing purposes.

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SANITATION

- Workers subject to skin contact with barium oxide or liquids containing barium oxide should wash any areas of the body which may have contacted barium oxide at the end of each work day.

- Skin that becomes contaminated with barium carbonate, barium chloride, or barium nitrate should be promptly washed or showered to remove any contaminant. In the case of barium carbonate, employees should use soap or mild detergent and water for washing purposes.

- Skin that becomes contaminated with barium oxide should be promptly washed or showered to remove any barium oxide from the skin after all obvious amounts of barium oxide have been removed by other means (e.g., by use of oil or vaseline). Employees who are being burned by barium oxide should immediately utilize quick drenching facilities without first removing barium oxide by other means.
- Eating and smoking should not be permitted in areas where solid barium carbonate, barium chloride, barium nitrate, or barium oxide, or liquids containing these compounds are handled, processed, or stored.
- Employees who handle barium carbonate, barium chloride, barium nitrate, barium oxide, or liquids containing these compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities. In the case of barium carbonate, employees should use soap or mild detergent and water for washing purposes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble barium compounds may occur and control methods which may be effective in each case:

Operation	Controls
Manufacture and distribution of soluble barium compounds	Process enclosure; local exhaust ventilation
Use in manufacture of pressed and blown glassware and flint and crown optical glass; manufacture of ceramic products; use in electronics industry in manufacture of magnets, vacuum tubes, cathodes, x-ray fluorescent screens, TV picture tubes, and dry cell depolarizers	Process enclosure; local exhaust ventilation
Use in manufacture of photographic papers, dyes, and chemicals	Process enclosure; local exhaust ventilation
Use as pesticides, rodenticides, and disinfectants; use in manufacture of explosives, matches, and pyrotechnics as igniter compositions and fireworks	Process enclosure; local exhaust ventilation

Operation

Use as an additive in manufacture of grease, and manufacture of lubricating oils; use in refining of vegetable and animal oils

Use in case-hardening of steel in metallurgy; in welding aluminum; in electroplating; and in aluminum and sodium refining

Use in water treatment and boiler compounds for softening water; use as catalysts, analytical reagents, and purifying agents

Use for treatment of textiles, leather, and rubber; use in manufacture of paper and cellulose as a bleaching agent; use in manufacture of pigments, colors, and lakes

Use as a depilatory in processing of hides; as a fire-proof and extinguishing agent; in embalming; in sugar refining; in gas and solvent drying; in marble substitutes; in valve manufacture; and as a smoke suppressant in diesel fuels

Use in manufacture of pigments, paints, enamels, and printing inks

Controls

Process enclosure;
local exhaust ventilation

Process enclosure;
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Process enclosure;
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Process enclosure;
local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If solutions of barium compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

- Skin that becomes contaminated with barium oxide should be promptly washed or showered to remove any barium oxide from the skin after all obvious amounts of barium oxide have been removed by other means (e.g., by use of oil or vaseline). Employees who are being burned by barium oxide should immediately utilize quick drenching facilities without first removing barium oxide by other means.
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Use in manufacture of photographic papers, dyes, and chemicals	Process enclosure; local exhaust ventilation
Use as pesticides, rodenticides, and disinfectants; use in manufacture of explosives, matches, and pyrotechnics as igniter compositions and fireworks	Process enclosure; local exhaust ventilation
Use as an additive in manufacture of grease, and manufacture of lubricating oils; use in refining of vegetable and animal oils	Process enclosure; local exhaust ventilation
Use in case-hardening of steel in metallurgy; in welding aluminum; in electroplating; and in aluminum and sodium refining	Process enclosure; local exhaust ventilation
Use in water treatment and boiler compounds for softening water; use as catalysts, analytical reagents, and purifying agents	Process enclosure; local exhaust ventilation
Use for treatment of textiles, leather, and rubber; use in manufacture of paper and cellulose as a bleaching agent; use in manufacture of pigments, colors, and lakes	Process enclosure; local exhaust ventilation
Use as a depilatory in processing of hides; as a fire-proof and extinguishing agent; in embalming; in sugar refining; in gas and solvent drying; in marble substitutes; in valve manufacture; and as a smoke suppressant in diesel fuels	Process enclosure; local exhaust ventilation
Use in manufacture of pigments, paints, enamels, and printing inks	Process enclosure; local exhaust ventilation

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In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If solutions of barium compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If solutions of barium compounds get on the skin, immediately flush the contaminated skin with water. If solutions of barium compounds soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of soluble barium compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When soluble barium compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If soluble barium compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.

2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquids containing soluble barium compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- **Waste disposal method:**

Soluble barium compounds may be disposed of in sealed containers in a secured sanitary landfill.

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- **Skin Exposure**

If solutions of barium compounds get on the skin, immediately flush the contaminated skin with water. If solutions of barium compounds soak through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of soluble barium compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When soluble barium compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If soluble barium compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.

2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquids containing soluble barium compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- **Waste disposal method:**

Soluble barium compounds may be disposed of in sealed containers in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR SOLUBLE BARIUM COMPOUNDS (AS BARIUM)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m ³
Particulate Concentration	
2.5 mg/m ³ or less	Any dust and mist respirator, except single-use.**
5 mg/m ³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
25 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m ³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode. A powered air-purifying respirator with a high efficiency particulate filter.
Greater than 250 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

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Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m ³
Particulate Concentration	
2.5 mg/m ³ or less	Any dust and mist respirator, except single-use.**
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Occupational Health Guideline for Cadmium Dust (as Cadmium)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all cadmium dust. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Cadmium metal dust

- Formula: Cd
- Synonyms: None
- Appearance and odor: Odorless, gray powder.

Cadmium oxide dust

- Formula: CdO
- Synonyms: None
- Appearance and odor: Odorless, brown solid or blue-black solid.

Cadmium sulfide dust

- Formula: CdS
- Synonyms: Greenockite
- Appearance: Yellow-orange solid.

Cadmium chloride dust

- Formula: CdCl₂
- Synonyms: None
- Appearance: White solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cadmium dust is 0.2 milligram of cadmium dust per cubic meter of air (mg/m³) averaged over an eight-hour work shift, with a ceiling level of 0.6 mg/m³. NIOSH has recommended that the permissible exposure limit be reduced to 40 micrograms of cadmium per cubic meter of air (μg/m³) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 200 μg/m³ averaged over a 15-minute period. The recommendations in this guideline supplement the recommendations in the NIOSH Criteria Document for Cadmium, which should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Cadmium dust can affect the body if it is inhaled. It can also affect the body if it is swallowed.

• Effects of overexposure

1. *Short-term Exposure:* Cadmium dust may cause irritation of the nose and throat. If enough has been inhaled, after a delay of several hours, a person may also develop cough, chest pain, sweating, chills, shortness of breath, and weakness. Death may occur. Ingestion of cadmium dust may cause nausea, vomiting, diarrhea, and abdominal cramps.

2. *Long-term Exposure:* Repeated or prolonged exposure to cadmium dust may cause loss of sense of smell, ulceration of the nose, shortness of breath (emphysema), kidney damage, and mild anemia. Exposure to cadmium has also been reported to cause an increased incidence of cancer of the prostate in man. Injections of cadmium sulfate in animals have been reported to cause malformation in their offspring.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cadmium dust.

• Recommended medical surveillance

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
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The following medical procedures should be made available to each employee who is exposed to cadmium dust at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, liver, kidneys, prostate, and blood should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to cadmium, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. In addition, the urine should be examined for low molecular weight proteins by use of 3% sulfosalicylic or other acceptable techniques.

—14" x 17" chest roentgenogram: Cadmium causes human lung damage. Surveillance of the lungs is indicated.

—Liver function tests: Cadmium may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—FVC and FEV (1 sec): Cadmium is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease. Urine protein measurements should be made available every four months.

• Summary of toxicology

Cadmium dust causes both acute and chronic effects. It is less toxic than cadmium fume, because dust has a larger particle size than fume; at high concentrations of the dust, physiologic effects similar to those arising from fume exposure could be expected. The acute effects primarily involve the lungs but may also affect other organ systems. Most acute intoxications have been caused by inhalation of cadmium fume at concentrations which did not provide warning symptoms of irritation. The average concentrations of fume responsible for fatalities have been 40 to 50 mg/m³ for 1 hour, or 9 mg/m³ for 5 hours. Non-fatal pneumonitis has been reported from concentrations of 0.5 to 2.5 mg/m³, while relatively mild cases have been attributed to even lower concentrations. Following an asymptomatic latent period of 4 to 10 hours, there is characteristic nasopharyngeal irritation followed by a feeling of chest constriction or substernal pain, with persistent cough and dyspnea; there may also be headache, chills, muscle aches, nausea, vomiting, and diarrhea. Pulmonary edema may then develop and progress rapidly, with decreased vital capacity and markedly reduced carbon monoxide diffusing capacity. Cyanosis may be intense. In about 20% of the cases the dyspnea is progressive,

accompanied by wheezing or hemoptysis, and may result in death within 7 to 10 days after exposure; at autopsy the lungs are markedly congested, and there is an intra-alveolar fibrinous exudate, as well as alveolar cell metaplasia. Among survivors, the subsequent course is unpredictable: most cases resolve slowly, but respiratory symptoms may linger for several weeks, while impairment of pulmonary function may persist for months. In experimental animals, cadmium exposure has caused pulmonary fibrosis, but this has not been documented in humans. In one fatal human case, in addition to lung abnormalities, there was renal cortical necrosis. Absorbed cadmium is retained to a large extent by the body, and excretion is very slow. Continued exposure to low levels of cadmium in air has resulted in chronic poisoning characterized by irreversible lung injury of an emphysematous type, with abnormal lung function and urinary excretion of a specific low-molecular-weight protein which may be associated with renal dysfunction. Clinical evidence of the cumulative effects of cadmium may appear after exposure has terminated; the disease then tends to be progressive. The frequency of occurrence of proteinuria increases with length of exposure: those exposed to cadmium compounds for less than 2 years had no proteinuria, whereas most of those exposed for 12 years or more had proteinuria with little other evidence of renal damage. The urinary excretion of cadmium bears no known relationship to the severity or duration of exposure and is only a confirmation of absorption. Other consequences of cadmium exposure are rhinitis, occasional ulceration of the nasal septum, damage to the olfactory nerve, and anosmia. The long-term ingestion of water, beans, and rice contaminated with cadmium has been proposed as the probable cause of a crippling condition among Japanese women who have had multiple pregnancies; severe pain in the back and joints, a waddly gait, osteomalacia, spontaneous fractures, and occasional fatal renal failure are characteristics of the disorder, which has been termed "itai-itai." Subcutaneous injection of cadmium metal suspended in fowl serum produced rhabdomyosarcomata in rats; cadmium sulfate in sterile distilled water produced sarcomata; and cadmium chloride solution produced pleomorphic sarcomata at the injection site. Increased incidence of prostatic cancer has been reported following occupational exposure to cadmium. Cadmium sulfate injected into the lingual vein of female hamsters on day 8 of pregnancy caused a high incidence of resorption and malformed offspring; acute necrosis of rat testes follows large doses orally or parenterally, but testicular effects have not been reported in humans.

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CHEMICAL AND PHYSICAL PROPERTIES

• Physical data—Cadmium metal dust

1. Molecular weight: 112.4
2. Boiling point (760 mm Hg): 767 C (1412 F)
3. Specific gravity (water = 1): 8.642
4. Vapor density (air = 1 at boiling point of cadmium metal dust): Not applicable
5. Melting point: 321 C (609 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Cadmium oxide dust

1. Molecular weight: 128.4
2. Boiling point (760 mm Hg): 900 C (1652 F) (sublimes and decomposes)
3. Specific gravity (water = 1): 6.95 or 8.15
4. Vapor density (air = 1 at boiling point of cadmium oxide dust): Not applicable
5. Melting point: 900 C (1652 F) (sublimes and decomposes)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0005
8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Cadmium sulfide dust

1. Molecular weight: 144.5
2. Boiling point (760 mm Hg): Sublimes in N₂ at 980 C (1796 F)
3. Specific gravity (water = 1): 4.82
4. Vapor density (air = 1 at boiling point of cadmium sulfide dust): Not applicable
5. Melting point: 1750 C (3182 F) at 100 atm.
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.0001
8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Cadmium chloride dust

1. Molecular weight: 183
2. Boiling point (760 mm Hg): 960 C (1760 F)
3. Specific gravity (water = 1): 4.047
4. Vapor density (air = 1 at boiling point of cadmium chloride dust): Not applicable
5. Melting point: 568 C (1054 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 140
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact of cadmium metal dust with strong oxidizers or with elemental sulfur, selenium, and tellurium may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as cadmium oxide fume) may be released in a fire involving cadmium dust.

4. Special precautions: None

• Flammability

1. Flash point: Not applicable
2. Autoignition temperature: 250 C (482 F) (layer) (cadmium metal dust)
3. Minimum explosive dust concentration: Data not available
4. Extinguishant: Dry powder for metal fires

• Warning properties

Grant states that "cadmium is a very toxic metal which gives off fumes when burned or heated strongly. Characteristically these fumes cause dryness and irritation of the throat, followed in a few hours by nausea and diarrhea. Smarting of the eyes occurs relatively infrequently, and no injury to the eyes of human beings has been reported. Neither eye nor respiratory irritation is enough to prevent exposures which may cause serious systemic poisoning and damage to the lungs."

MONITORING AND MEASUREMENT PROCEDURES

• Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of cadmium dust. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of cadmium dust on a filter, followed by treatment with nitric acid, solution in hydrochloric acid, and atomic absorption spectrophotometric analysis. An analytical method for cadmium dust is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

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• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of cadmium dust. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of cadmium dust on a filter, followed by treatment with nitric acid, solution in hydrochloric acid, and atomic absorption spectrophotometric analysis. An analytical method for cadmium dust is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- If employees' clothing has had any possibility of being contaminated with cadmium dust, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with cadmium dust should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cadmium dust from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cadmium dust, the person performing the operation should be informed of cadmium dust's hazardous properties.
- Employees should be provided with and required to use dust-resistant safety goggles where there is any possibility of cadmium chloride dust contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to cadmium chloride dust, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Workers subject to skin contact with cadmium dust should wash with soap or mild detergent and water any areas of the body which may have contacted cadmium dust at the end of each work day.
- Eating and smoking should not be permitted in areas where cadmium dust is handled, processed, or stored.
- Employees who handle cadmium dust should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cadmium dust may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from fabrication of cadmium-plated marine, aircraft, and motor vehicle equipment for corrosion-resistant coatings	Local exhaust ventilation; personal protective equipment
Liberation during processing of cadmium metal	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation in synthesis of cadmium compounds	Process enclosure; local exhaust ventilation
Liberation in manufacture and fabrication of cadmium alloys; recovery from flue dusts during smelting of lead and zinc operations	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of nuclear reactor rods	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If cadmium dust gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If cadmium dust gets on the skin, wash the contaminated skin using soap or mild detergent and water. Be sure to wash the hands well before eating or smoking and at the close of work.

• Breathing

If a person breathes in large amounts of cadmium dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When cadmium dust or liquids containing cadmium dust have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the

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person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If cadmium dust is released in hazardous concentrations, the following steps should be taken:
 1. Remove all ignition sources.
 2. Ventilate area of release.
 3. Collect released material in the most convenient and safe manner for reclamation or for disposal in sealed containers in a secured sanitary landfill.
- Waste disposal method:
Cadmium dust may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Cadmium Dust," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 11, 1976.

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RESPIRATORY PROTECTION FOR CADMIUM DUST (AS CADMIUM)

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m ³
Dust Concentration	
1 mg/m ³ or less	Any dust respirator, except single-use.
2 mg/m ³ or less	Any dust respirator, except single-use or quarter-mask respirator. Any high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
10 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m ³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Cadmium Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Cd/CdO
- Synonyms: None
- Appearance: Finely divided solid particles dispersed in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cadmium fume is 0.1 milligram of cadmium fume per cubic meter of air (mg/m^3) averaged over an eight-hour work shift, with an acceptable ceiling level of $0.3 \text{ mg}/\text{m}^3$. NIOSH has recommended that the permissible exposure limit be reduced to a time-weighted average of 40 micrograms cadmium per cubic meter (ug/m^3) with a ceiling level of $200 \text{ ug cadmium}/\text{m}^3$ for a 15-minute period. The NIOSH Criteria Document for Cadmium should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Cadmium fume can affect the body if it is inhaled.

• Effects of overexposure

1. *Short-term Exposure:* Cadmium fume causes irritation of the nose and throat. If enough has been inhaled, after a delay of several hours, a person may also develop cough, chest pain, sweating, chills, shortness of breath, and weakness. Death may occur.

2. *Long-term Exposure:* Repeated or prolonged exposure to cadmium fume may cause loss of sense of smell, ulceration of the nose, shortness of breath (emphyse-

ma), kidney damage, and mild anemia. Exposure to cadmium fume has also been reported to cause an increased incidence of cancer of the prostate in men. Injections of cadmium sulfate in animals have been reported to cause malformation in their offspring. This effect has not been reported in humans.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cadmium fume.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to cadmium fume at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, kidneys, and blood should be stressed.

—Urinalysis: Since kidney damage has been observed in humans exposed to cadmium, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The urine should be examined for the specific protein.

—14" x 17" chest roentgenogram: Cadmium causes human lung damage. Surveillance of the lungs is indicated.

—Liver function tests: Cadmium may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—FVC and FEV (1 sec): Cadmium is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

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Urine protein measurements should be made available every four months.

- **Summary of toxicology**

Cadmium fume (cadmium oxide) is a severe pulmonary irritant that has caused fatal pulmonary edema in workers; chronic exposures may lead to severe pulmonary emphysema. Cadmium sulfide produces malignant tumors in animals by injection, suggesting that cadmium is carcinogenic. Most acute intoxications have been caused by inhalation of cadmium fume at concentrations which did not provide warning symptoms of irritation. The average concentrations of fume responsible for fatalities have been 40 to 50 mg/m³ for 1 hour, or 9 mg/m³ for 5 hours. Non-fatal pneumonitis has been reported from concentrations of 0.5 to 2.5 mg/m³, while relatively mild cases have been attributed to even lower concentrations. Following an asymptomatic latent period of 4 to 10 hours, there is characteristically nasopharyngeal irritation, followed by a feeling of chest constriction or substernal pain, with cough and dyspnea; there also may be headache, chills, muscle aches, nausea, vomiting, and diarrhea. Pulmonary edema may then develop rapidly, with decreased vital capacity and markedly reduced carbon monoxide diffusing capacity. In about 20% of the cases the dyspnea is progressive, accompanied by wheezing or hemoptysis, and may result in death within 7 to 10 days of exposure; at autopsy the lungs are markedly congested, and there is an intra-alveolar fibrinous exudate, as well as alveolar cell metaplasia. Among survivors, the subsequent course is unpredictable: most cases resolve slowly, but respiratory symptoms may linger for several weeks, while impairment of pulmonary function may persist for months. In experimental animals, cadmium exposure has caused pulmonary fibrosis, but this has not been documented in humans. In one fatal human case, in addition to lung abnormalities, there was renal cortical necrosis. Continued exposure to lower levels of cadmium in air has resulted in chronic poisoning characterized by irreversible lung injury of emphysematous type, with abnormal lung function and urinary excretion of a specific low-molecular-weight protein which may be associated with evidence of renal dysfunction. Clinical evidence of the cumulative effects of cadmium may appear after exposure has terminated; the disease then tends to be progressive. The frequency of occurrence of proteinuria increases with length of exposure: those exposed to cadmium compounds for less than 2 years had no proteinuria, whereas most of those exposed for 12 years or more had proteinuria with little other evidence of renal damage. Cadmium absorbed by any route is, to a very large extent, retained by the body. Excretion is very slow. The urinary excretion of cadmium bears no known relationship to the severity or duration of exposure and is only a confirmation of absorption. Other consequences of cadmium exposure are rhinitis, occasional ulceration of the nasal septum, damage to the olfactory nerve, and anosmia. The long-term ingestion of beans, rice and water contaminated

with cadmium has been proposed as the probable cause of a crippling condition among Japanese women who have had multiple pregnancies; pain in the back and joints, an unsteady gait, osteomalacia, bone fractures, and occasional renal failure are characteristics of the disorder. Rats, injected subcutaneously with cadmium metal suspended in fowl serum, produced rhabdomyosarcomata; with cadmium sulfate in sterile distilled water, sarcomata; and with cadmium chloride solution, pleomorphic sarcomas at the injection site, suggesting that cadmium is carcinogenic. Cadmium sulfate injected into the lingual vein of female hamsters on day 8 of pregnancy caused a high incidence of resorption and malformed offspring. Increased prostatic and lung cancer has been reported in humans exposed to cadmium oxide. Acute necrosis of the rat testis follows large doses orally or parenterally.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 112 – 128
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of cadmium fume): Not applicable
5. Melting point: Not applicable
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Not applicable

- **Flammability**

1. Not applicable

- **Warning properties**

Grant reports that "smarting of the eyes occurs relatively infrequently (upon exposure to cadmium fume), and no injury to the eyes of human beings has been reported. Neither eye nor respiratory tract irritation is enough to prevent exposures which may cause serious systemic poisoning and damage to the lungs."

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected

Urine protein measurements should be made available every four months.

- **Summary of toxicology**

Cadmium fume (cadmium oxide) is a severe pulmonary irritant that has caused fatal pulmonary edema in workers; chronic exposures may lead to severe pulmonary emphysema. Cadmium sulfide produces malignant tumors in animals by injection, suggesting that cadmium is carcinogenic. Most acute intoxications have been caused by inhalation of cadmium fume at concentrations which did not provide warning symptoms of irritation. The average concentrations of fume responsible for fatalities have been 40 to 50 mg/m³ for 1 hour, or 9 mg/m³ for 5 hours. Non-fatal pneumonitis has been reported from concentrations of 0.5 to 2.5 mg/m³, while relatively mild cases have been attributed to even lower concentrations. Following an asymptomatic latent period of 4 to 10 hours, there is characteristically nasopharyngeal irritation, followed by a feeling of chest constriction or substernal pain, with cough and dyspnea; there also may be headache, chills, muscle aches, nausea, vomiting, and diarrhea. Pulmonary edema may then develop rapidly, with decreased vital capacity and markedly reduced carbon monoxide diffusing capacity. In about 20% of the cases the dyspnea is progressive, accompanied by wheezing or hemoptysis, and may result in death within 7 to 10 days of exposure; at autopsy the lungs are markedly congested, and there is an intra-alveolar fibrinous exudate, as well as alveolar cell metaplasia. Among survivors, the subsequent course is unpredictable: most cases resolve slowly, but respiratory symptoms may linger for several weeks, while impairment of pulmonary function may persist for months. In experimental animals, cadmium exposure has caused pulmonary fibrosis, but this has not been documented in humans. In one fatal human case, in addition to lung abnormalities, there was renal cortical necrosis. Continued exposure to lower levels of cadmium in air has resulted in chronic poisoning characterized by irreversible lung injury of emphysematous type, with abnormal lung function and urinary excretion of a specific low-molecular-weight protein which may be associated with evidence of renal dysfunction. Clinical evidence of the cumulative effects of cadmium may appear after exposure has terminated; the disease then tends to be progressive. The frequency of occurrence of proteinuria increases with length of exposure: those exposed to cadmium compounds for less than 2 years had no proteinuria, whereas most of those exposed for 12 years or more had proteinuria with little other evidence of renal damage. Cadmium absorbed by any route is, to a very large extent, retained by the body. Excretion is very slow. The urinary excretion of cadmium bears no known relationship to the severity or duration of exposure and is only a confirmation of absorption. Other consequences of cadmium exposure are rhinitis, occasional ulceration of the nasal septum, damage to the olfactory nerve, and anosmia. The long-term ingestion of beans, rice and water contaminated

with cadmium has been proposed as the probable cause of a crippling condition among Japanese women who have had multiple pregnancies; pain in the back and joints, an unsteady gait, osteomalacia, bone fractures, and occasional renal failure are characteristics of the disorder. Rats, injected subcutaneously with cadmium metal suspended in fowl serum, produced rhabdomyosarcomata; with cadmium sulfate in sterile distilled water, sarcomata; and with cadmium chloride solution, pleomorphic sarcomas at the injection site, suggesting that cadmium is carcinogenic. Cadmium sulfate injected into the lingual vein of female hamsters on day 8 of pregnancy caused a high incidence of resorption and malformed offspring. Increased prostatic and lung cancer has been reported in humans exposed to cadmium oxide. Acute necrosis of the rat testis follows large doses orally or parenterally.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 112 — 128
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of cadmium fume): Not applicable
5. Melting point: Not applicable
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Not applicable

- **Flammability**

1. Not applicable

- **Warning properties**

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Measurements to determine employee ceiling exposure are best taken during periods of maximum expected

airborne concentrations of cadmium fume. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of cadmium fume on a cellulose membrane filter, followed by treatment with nitric acid, solution in acid, and analysis with an atomic absorption spectrophotometer. An analytical method for cadmium fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

SANITATION

• Eating and smoking should not be permitted in areas where fumes may be generated in the handling or processing of cadmium.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cadmium fume may occur and control methods which may be effective in each case:

Operation

Controls

Liberation during smelting and refining of ores where it is a by-product of zinc, lead, and copper-bearing ores

Process enclosure; local exhaust ventilation; personal protective equipment

Liberation during recovery of metal by processing of scrap; during melting and pouring of cadmium metal; during casting of alloys for cadmium-copper, cadmium-lead, cadmium-bismuth, cadmium-silver, cadmium-nickel, cadmium-lead-silver, cadmium-lead-silver-nickel, cadmium-lead-bismuth-tin, and cadmium-gold products used for coating telephone cables, trolley wires, welding electrodes, automatic sprinkling systems, steam boilers, fire alarms, high-pressure/temperature bearings, starting switches, aircraft relays, light-duty circuit breakers, low-temperature solder, and jewelry

Process enclosure; local exhaust ventilation; personal protective equipment

Liberation during fabrication of metal, alloys, or plated steel

Process enclosure; local exhaust ventilation; personal protective equipment

Liberation during casting and use of solders; during melting of cadmium ingots for paint and pigment manufacture used for coloring of plastics and ceramic glazes, electroplating, and in chemical synthesis

Process enclosure; local exhaust ventilation; personal protective equipment

Liberation during coating on metals by hot dipping or spraying

Process enclosure; local exhaust ventilation; personal protective equipment

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Liberation during fabrication of metal, alloys, or plated steel

Liberation during casting and use of solders; during melting of cadmium ingots for paint and pigment manufacture used for coloring of plastics and ceramic glazes, electroplating, and in chemical synthesis

Liberation during coating on metals by hot dipping or spraying

Controls

Process enclosure; local exhaust ventilation; personal protective equipment

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Liberation during manufacture of nickel-cadmium batteries for use in radio-portable telephones, convenience appliances, and vented cells used in air planes, helicopters, and stand-by power and lighting

Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Breathing

If a person breathes in large amounts of cadmium fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of cadmium fume are inadvertently released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Cadmium and Compounds as Cd," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 11, 1976.

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RESPIRATORY PROTECTION FOR CADMIUM FUME

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m ³
Particulate Concentration	
1 mg/m ³ or less	Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
40 mg/m ³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 40 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Chromium Metal and Insoluble Chromium Salts*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all chromium metal and insoluble chromium salts. Physical and chemical properties of some specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Metallic chromium

- Formula: Cr
- Synonyms: None
- Appearance and odor: Shiny, odorless metal.

Copper chromite

- Formula: $\text{Cu}_2\text{Cr}_2\text{O}_4$
- Synonyms: Cuprous chromite
- Appearance and odor: Greenish-blue, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chromium metal or insoluble chromium salts is 1 milligram of chromium metal or insoluble chromium salts per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: The non-carcinogenic forms are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium,

cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to $0.001 \text{ Cr (VI) mg}/\text{m}^3$ and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to $0.025 \text{ Cr (VI) mg}/\text{m}^3$ averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of $0.05 \text{ Cr (VI) mg}/\text{m}^3$ averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Chromium metal or insoluble chromium salts can affect the body if they are inhaled. They can also affect the body if they are swallowed.

• Effects of overexposure

Ferro chrome alloys have been associated with lung changes in workers exposed to these alloys. Chromite dust exposure may cause minor lung changes.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chromium metal or insoluble chromium salts.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to chromium metal or insoluble chromium salts at potentially hazardous levels:

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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U.S. DEPARTMENT OF LABOR

Occupational Safety and Health Administration

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Chromium and its insoluble salts may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Insoluble chromium salts are reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• Summary of toxicology

The dusts of chromium metal and its insoluble salts, chiefly the chromites, are usually reported to be relatively nontoxic; this is debatable, since exposures associated with toxic effects are usually mixed exposures involving several hexavalent chromium compounds. Ferrochrome alloys have been associated with pulmonary disease in humans. Four workers engaged in the production of ferrochrome alloys developed a nodular type of pulmonary disease with impairment of pulmonary function; air concentrations of chromium in this study averaged 0.26 mg/m³, although other fumes and dusts were also present. This pulmonary problem may be one of hypersensitivity and thus reversible. Other reports state that chest roentgenograms have revealed only "exaggerated pulmonic markings" in workers exposed to chromite dust. The lungs of groups of workers exposed to chromite dust have been shown to be the seat of pneumoconiotic changes consisting of slight thickening of interstitial tissue and interalveolar septa, with histologic fibrosis and hyalinization. Chromite ore roast mixed with sheep fat implanted intrapleurally in rats produced squamous cell carcinomata coexisting with sarcomata of the lungs; the same material implanted in the thighs of rats produced fibrosarcomata. A refractory plant using chromite ore to make chromite brick had no excess of lung cancer deaths over a 14-year period, and it was concluded that chromite alone probably is not carcinogenic.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data—Metallic chromium

1. Molecular weight: 52
2. Boiling point (760 mm Hg): 2640 C (4784 F)
3. Specific gravity (water = 1): 7.2
4. Vapor density (air = 1 at boiling point of metallic chromium): Not applicable
5. Melting point: 1900 C (3452 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Copper chromite

1. Molecular weight: 295.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 5.24
4. Vapor density (air = 1 at boiling point of copper chromite): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Basic potassium zinc chromate

1. Molecular weight: 873.8
2. Boiling point (760 mm Hg): Decomposes at red heat
3. Specific gravity (water = 1): 3.47
4. Vapor density (air = 1 at boiling point of basic potassium zinc chromate): Not applicable
5. Melting point: Loses water slowly above 100 C (212 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: Chromium metal in contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None listed.
4. Special precautions: None listed.

• Flammability

1. Flash point: Not applicable
2. Minimum ignition temperature (metal): 400 C (752 F) (layer); 580 C (1076 F) (cloud)
3. Minimum explosive dust concentration (metal): 230 grams/m³
4. Extinguishant: Dry sand, dry dolomite, dry graphite

• Warning properties

Chromium metal and insoluble salts are not known to be eye irritants.

MONITORING AND MEASUREMENT PROCEDURES

• Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Chromium and its insoluble salts may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Insoluble chromium salts are reported to cause decreased pulmonary function. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

• Summary of toxicology

The dusts of chromium metal and its insoluble salts, chiefly the chromites, are usually reported to be relatively nontoxic; this is debatable, since exposures associated with toxic effects are usually mixed exposures involving several hexavalent chromium compounds. Ferrochrome alloys have been associated with pulmonary disease in humans. Four workers engaged in the production of ferrochrome alloys developed a nodular type of pulmonary disease with impairment of pulmonary function; air concentrations of chromium in this study averaged 0.26 mg/m³, although other fumes and dusts were also present. This pulmonary problem may be one of hypersensitivity and thus reversible. Other reports state that chest roentgenograms have revealed only "exaggerated pulmonic markings" in workers exposed to chromite dust. The lungs of groups of workers exposed to chromite dust have been shown to be the seat of pneumoconiotic changes consisting of slight thickening of interstitial tissue and interalveolar septa, with histologic fibrosis and hyalinization. Chromite ore roast mixed with sheep fat implanted intrapleurally in rats produced squamous cell carcinomata coexisting with sarcomata of the lungs; the same material implanted in the thighs of rats produced fibrosarcomata. A refractory plant using chromite ore to make chromite brick had no excess of lung cancer deaths over a 14-year period, and it was concluded that chromite alone probably is not carcinogenic.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data—Metallic chromium

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2. Boiling point (760 mm Hg): 2640 C (4784 F)
3. Specific gravity (water = 1): 7.2
4. Vapor density (air = 1 at boiling point of metallic chromium): Not applicable
5. Melting point: 1900 C (3452 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

2 Chromium Metal and Insoluble Chromium Salts (as Chromium)

• Physical data—Copper chromite

1. Molecular weight: 295.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 5.24
4. Vapor density (air = 1 at boiling point of copper chromite): Not applicable
5. Melting point: Data not available
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Basic potassium zinc chromate

1. Molecular weight: 873.8
2. Boiling point (760 mm Hg): Decomposes at red heat
3. Specific gravity (water = 1): 3.47
4. Vapor density (air = 1 at boiling point of basic potassium zinc chromate): Not applicable
5. Melting point: Loses water slowly above 100 C (212 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: Chromium metal in contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: None listed.
4. Special precautions: None listed.

• Flammability

1. Flash point: Not applicable
2. Minimum ignition temperature (metal): 400 C (752 F) (layer); 580 C (1076 F) (cloud)
3. Minimum explosive dust concentration (metal): 230 grams/m³
4. Extinguishant: Dry sand, dry dolomite, dry graphite

• Warning properties

Chromium metal and insoluble salts are not known to be eye irritants.

MONITORING AND MEASUREMENT PROCEDURES

• Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected

airborne concentrations of chromium metal or insoluble chromium salts. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of chromium metal or insoluble chromium salts on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for chromium metal and insoluble chromium salts is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solids or liquids containing insoluble chromium salts.

- Clothing contaminated with insoluble chromium salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of insoluble chromium salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the insoluble chromium salts, the person

performing the operation should be informed of insoluble chromium salts's hazardous properties.

- Non-impervious clothing which becomes contaminated with insoluble chromium salts should be removed promptly and not reworn until the insoluble chromium salts are removed from the clothing.

- Employees should be provided with and required to use dust- and splashproof safety goggles where solids or liquids containing insoluble chromium salts may contact the eyes.

SANITATION

- Skin that becomes contaminated with insoluble chromium salts should be promptly washed or showered with soap or mild detergent and water to remove any insoluble chromium salts.

- Eating and smoking should not be permitted in areas where solids or liquids containing insoluble chromium salts are handled, processed, or stored.

- Employees who handle solids or liquids containing insoluble chromium salts should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chromium metal or insoluble chromium salts may occur and control methods which may be effective in each case:

Operation	Controls
Use in fabrication of alloys	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in preparation of alloy steels to enhance corrosion- and heat-resistance	Local exhaust ventilation; general dilution ventilation
Use in fabrication of plated products for decoration or increased wear-resistance	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in production of non-ferrous alloys to impart special qualities to the alloys	Local exhaust ventilation; general dilution ventilation
Use in production and processing of insoluble salts	Local exhaust ventilation; general dilution ventilation; personal protective equipment

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- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solids or liquids containing insoluble chromium salts.

- Clothing contaminated with insoluble chromium salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of insoluble chromium salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the insoluble chromium salts, the person

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Operation	Controls
Use as chemical intermediates; use in textile industry in dyeing, silk treating, printing, and moth-proofing wool	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in leather industry in tanning; use in photographic fixing baths	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as catalysts for halogenation, alkylation, and catalytic cracking of hydrocarbons	Local exhaust ventilation; general dilution ventilation
Use as fuel additives and propellant additives; in photographic fixing baths and in ceramics	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If chromium metal or solids or liquids containing insoluble chromium salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

• Skin Exposure

If solids or liquids containing insoluble chromium salts get on the skin, wash the contaminated skin using soap or mild detergent and water. If solids or liquids containing insoluble chromium salts penetrate through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of chromium metal or insoluble chromium salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When solids or liquids containing insoluble chromium salts have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If chromium metal or insoluble chromium salts are spilled, the following steps should be taken:

1. Remove all ignition sources where metallic chromium has been spilled.
2. Ventilate area of spill.
3. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing chromium metal or insoluble chromium salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Chromium metal or insoluble chromium salts may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Chromium (as Cr)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Brownning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
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- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- Hueper, W. C.: "Experimental Studies in Metal Carcinogenesis. X. Cancerigenic Effects of Chromite Ore Roast Deposited in Muscle Tissue and Pleural Cavity of Rats," *A.M.A. Archives of Industrial Health*, 18:284-291, 1958.
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- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard Occupational Exposure to Chromium (VI)*, HEW Publication No. (NIOSH) 76-129, GPO No. 017-033-00125-1, U.S. Government Printing Office, Washington, D.C., 1975.

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- Thienes, C. H., and Haley, T. J.: *Clinical Toxicology* (5th ed.), Lea and Febiger, Philadelphia, 1972.

* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

• Method

Sampling and analyses may be performed by collection of chromium metal or insoluble chromium salts on a filter, followed by treatment with acid and atomic

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• Method

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RESPIRATORY PROTECTION FOR CHROMIUM METAL AND INSOLUBLE CHROMIUM SALTS (AS CHROMIUM)

Condition	Minimum Respiratory Protection* Required Above 1 mg/m ³
Particulate Concentration	
5 mg/m ³ or less	Any dust and mist respirator.
10 mg/m ³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m ³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Condition	Minimum Respiratory Protection* Required Above 1 mg/m ³
Particulate Concentration	
5 mg/m ³ or less	Any dust and mist respirator.
10 mg/m ³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
500 mg/m ³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Soluble Chromic and Chromous Salts (as Chromium)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble chromic and chromous salts. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Chromic sulfate hydrate

- Formula: $\text{Cr}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (approximately)
- Synonyms: None
- Appearance and odor: Violet or green, odorless solid.

Chromic potassium sulfate

- Formula: $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
- Synonyms: Potassium chrome alum; potassium chromium (III) sulfate
- Appearance and odor: Red-violet, odorless solid.

Chromous chloride

- Formula: CrCl_2
- Synonyms: None
- Appearance and odor: Colorless to gray, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble chromic or chromous salts is 0.5 milligrams of soluble chromic or

chromous salts (as chromium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: They are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to $0.001 \text{ mg}/\text{m}^3$ and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to $0.025 \text{ Cr (VI) mg}/\text{m}^3$ averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of $0.05 \text{ Cr (VI) mg}/\text{m}^3$ averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Soluble chromic or chromous salts can affect the body if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

• Effects of overexposure

Exposure to certain soluble chromic or chromous salts have been reported to cause an allergic skin rash.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble chromic or chromous salts.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Occupational Health Guideline for Soluble Chromic and Chromous Salts (as Chromium)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble chromic and chromous salts. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Chromic sulfate hydrate

- Formula: $\text{Cr}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (approximately)
- Synonyms: None
- Appearance and odor: Violet or green, odorless solid.

Chromic potassium sulfate

- Formula: $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
- Synonyms: Potassium chrome alum; potassium chromium (III) sulfate
- Appearance and odor: Red-violet, odorless solid.

Chromous chloride

- Formula: CrCl_2
- Synonyms: None
- Appearance and odor: Colorless to gray, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for soluble chromic or chromous salts is 0.5 milligrams of soluble chromic or

chromous salts (as chromium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: They are the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to $0.001 \text{ mg}/\text{m}^3$ and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to $0.025 \text{ Cr (VI) mg}/\text{m}^3$ averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of $0.05 \text{ Cr (VI) mg}/\text{m}^3$ averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Soluble chromic or chromous salts can affect the body if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

• Effects of overexposure

Exposure to certain soluble chromic or chromous salts have been reported to cause an allergic skin rash.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to soluble chromic or chromous salts.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to soluble chromic and chromous salts at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from soluble chromic and chromous salts exposure.

—Skin disease: Chromic salts may cause an allergic dermatitis. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

The soluble chromic and chromous salts have no established toxicity. Since exposures are often mixed, consideration should be given to the possible exposure to hexavalent chromium, which is a more toxic form. The compound hexaaquachromium trichloride has been found to react with protein in vitro, indicating that it is not biologically inert. Of 35 rats implanted with chromic acetate in the thigh muscle, 1 developed sarcoma; this was considered to be evidence of weak carcinogenicity of this soluble trivalent compound. When taken by mouth, the trivalent compounds do not give rise to local or systemic effects and are poorly absorbed; no specific effects are known to result from inhalation. Animals ingesting chromic salts showed one-ninth as much chromium in the tissues as did animals ingesting equal amounts of chromates. Dermatitis from some chromic salts has been reported. Some investigators believe that all persons sensitized to hexavalent chromium are also sensitive to the trivalent form, although this has not been firmly established.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Chromic sulfate hydrate**

1. Molecular weight: 680 (approximately)
2. Boiling point (760 mm Hg): Decomposes at red heat
3. Specific gravity (water = 1): 1.7
4. Vapor density (air = 1 at boiling point of chromic sulfate hydrate): Not applicable
5. Melting point: 90 C (194 F) Loses water, residue does not melt
6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): 84–120
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Chromic potassium sulfate**

1. Molecular weight: 499.4
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 1.83

4. Vapor density (air = 1 at boiling point of chromic potassium sulfate): Not applicable

5. Melting point: 89 C (192 F) Loses water, then melts at 400 C (752 F)

6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)

7. Solubility in water, g/100 g water at 20 C (68 F): 19.6

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Chromous chloride**

1. Molecular weight: 122.9

2. Boiling point (760 mm Hg): 1300 C (2372 F)

3. Specific gravity (water = 1): 2.93

4. Vapor density (air = 1 at boiling point of chromous chloride): Not applicable

5. Melting point: 820 C (1508 F)

6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)

7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Water (chromyl chloride)
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Most soluble chromic or chromous salts are not combustible. However, chromyl chloride reacts vigorously with water, forming chromic acid, chromic chloride, hydrochloric acid, and chlorine. Also, chromyl chloride causes ignition of ammonia, ethyl alcohol, turpentine, and other combustible materials.

- **Warning properties**

Grant states that "chromium compounds . . . are known to cause dermatitis, ulcers of the skin and mucous membranes, and perforation of the nasal septum." Chromium chloride is an example of the chromium compounds which Grant states produces these effects. Not all chromic and chromous salts produce eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of soluble chromic or chromous salts.

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3. Specific gravity (water = 1): 1.83

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5. Melting point: 89 C (192 F) Loses water, then melts at 400 C (752 F)

6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)

7. Solubility in water, g/100 g water at 20 C (68 F): 19.6

8. Evaporation rate (butyl acetate = 1): Not applicable

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1. Molecular weight: 122.9
2. Boiling point (760 mm Hg): 1300 C (2372 F)
3. Specific gravity (water = 1): 2.93
4. Vapor density (air = 1 at boiling point of chromous chloride): Not applicable

5. Melting point: 320 C (1508 F)

6. Vapor pressure at 20 C (68 F): Essentially zero (except water of crystallization)

7. Solubility in water, g/100 g water at 20 C (68 F): Very soluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Water (chromyl chloride)
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

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• Method

Sampling and analyses may be performed by collection of soluble chromic or chromous salts on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for soluble chromic and chromous salts is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquids or solids containing soluble chromic or chromous salts.

- Clothing contaminated with soluble chromic or chromous salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chromic or chromous salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chromic or chromous salts, the person performing the operation should be informed of soluble chromic or chromous salts's hazardous properties.

- Non-impervious clothing which becomes contaminated with soluble chromic or chromous salts should be removed promptly and not reworn until the soluble chromic or chromous salts are removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of liquids or solids containing soluble chromic or chromous salts contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to liquids or solids containing soluble chromic or chromous salts, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with soluble chromic or chromous salts should be promptly washed or showered to remove any soluble chromic or chromous salts.

- Employees who handle liquids or solids containing soluble chromic or chromous salts should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to soluble chromic or chromous salts may occur and control methods which may be effective in each case:

Operation	Controls
Use in textile treatment in dyeing, printing, moth-proofing, and water-proofing; use in tanning of leather in gloves, garments, and shoe uppers	Local exhaust ventilation; personal protective equipment
Use in manufacture of pigments for green varnishes, inks, paints, and glazes	Local exhaust ventilation; personal protective equipment
Use for metal treatment and polishing	Local exhaust ventilation; personal protective equipment
Use in photographic fixing baths for hardening of emulsions; use as catalysts and in manufacture of catalysts	Local exhaust ventilation; personal protective equipment
Use in chemical synthesis; use as corrosion inhibitors	Local exhaust ventilation; personal protective equipment

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Use in photographic fixing baths for hardening of emulsions; use as catalysts and in manufacture of catalysts	Local exhaust ventilation; personal protective equipment
Use in chemical synthesis; use as corrosion inhibitors	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquids or solids containing soluble chromic or chromous salts get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with these chemicals.

- **Skin Exposure**

If liquids or solids containing soluble chromic or chromous salts get on the skin, promptly flush the contaminated skin with water. If liquids or solids containing soluble chromic or chromous salts penetrate through the clothing, remove the clothing promptly and flush the skin with water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of soluble chromic or chromous salts, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When liquids or solids containing soluble chromic or chromous salts have been swallowed give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If soluble chromic or chromous salts are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing soluble chromic or chromous salts should be absorbed in vermiculite, dry sand, earth, or a similar material.

- **Waste disposal method:**

Soluble chromic or chromous salts may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Chromium (as Cr)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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4 Soluble Chromic and Chromous Salts (as Chromium)

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*** SPECIAL NOTE**

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

RESPIRATORY PROTECTION FOR SOLUBLE CHROMIC AND CHROMOUS SALTS (AS CHROMIUM)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m ³
Particulate Concentration	
2.5 mg/m ³ or less	Any dust and mist respirator, except single-use.**
5 mg/m ³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.** Any fume respirator or high efficiency particulate respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
25 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m ³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 250 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

RESPIRATORY PROTECTION FOR SOLUBLE CHROMIC AND CHROMOUS SALTS (AS CHROMIUM)

Condition	Minimum Respiratory Protection* Required Above 0.5 mg/m ³
Particulate Concentration	
2.5 mg/m ³ or less	Any dust and mist respirator, except single-use.**
5 mg/m ³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.** Any fume respirator or high efficiency particulate respirator.** Any supplied-air respirator.** Any self-contained breathing apparatus.**
25 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
250 mg/m ³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 250 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

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**If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

Occupational Health Guideline for Copper Dusts and Mists

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formulas of example compounds: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; CuCl
- Example compounds: Copper sulfate dust or mist; cuprous chloride dust
- Appearance and odor: Odorless solids

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for copper dusts or mists is 1 milligram of copper dusts or mists per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

• Routes of exposure

Copper dusts or mists can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

• Effects of overexposure

1. *Short-term Exposure:* Powdered copper or dusts or mists of copper salts may cause a feeling of illness similar to the common cold with sensations of chills and stuffiness of the head. Small copper particles may enter the eye and cause irritation, discoloration, and damage.

2. *Long-term Exposure:* Repeated or prolonged exposure to copper dusts or mists may cause skin irritation or discoloration of the skin or hair.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to copper dusts or mists.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to copper dusts and mists at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from copper dusts and mists exposure.

—Chronic respiratory disease: Copper dusts or mists cause respiratory irritation in animals. In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of copper dusts or mists might cause exacerbation of symptoms due to their irritant properties.

—Liver disease: Copper dusts or mists cause liver damage in animals. Persons with pre-existing liver disease may be more susceptible to the effects of these agents.

—Kidney disease: Copper dusts or mists cause kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: Skin sensitization in human subjects has occurred. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

—Hematopoietic disorders: Anemia has occurred in animals given copper salts orally. Persons with pre-existing blood disorders may be more susceptible to the effects of these agents.

—Wilson's disease: Persons with pre-existing Wilson's disease may be more susceptible to the effects of these agents.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

Inhalation of dusts and mists of copper and copper salts results in irritation of the upper respiratory tract, with occasional ulceration and perforation of the nasal septum. Inhalation of copper and its compounds by animals caused injury to the lungs and liver with

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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hemochromatosis. Access of sheep to salt licks containing 5 to 9% copper sulfate caused the sudden onset of hemolytic anemia, icterus, and hemoglobinuria followed by death in a day or two; at necropsy, the liver, kidneys, and spleen showed severe degenerative changes. Workers exposed to copper dust in concentrations of 0.075 to 0.120 mg/m³ complained of mild nasal discomfort. Exposure to the dust of copper acetate produced sneezing, coughing, digestive disorders, and fever. Metal workers exposed to complex copper salts in dust form complained of metallic taste with irritation of nasal and oral mucosa; atrophic changes in the mucous membranes were noted in subjects exposed for long periods of time. On ingestion, copper salts act as irritants and cause nausea, vomiting, abdominal pain, hemorrhagic gastritis, and diarrhea. Copper salts splashed in the eye cause conjunctivitis, corneal ulceration, and turbidity, and may produce palpebral edema. Copper particles embedded in the eye result in pronounced foreign-body reaction with characteristic discoloration of ocular tissue. Allergic contact dermatitis due to copper exposure, although rare, has been reported. Greenish discoloration of the skin and hair of some copper workers has been observed. Although copper is an essential element for health, excessive amounts can produce harmful effects.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: CuSO₄: 249.7; CuCl₂: 99
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of copper dusts or mists): Not applicable
5. Melting point: Higher than 100 C (212 F). For example, copper sulfate = 150 C (302 F); cuprous chloride = 430 C (806 F)
6. Vapor pressure at 20 C (68 F): Not applicable
7. Solubility in water, g/100 g water at 20 C (68 F): Ranges from very low (e.g. cuprous chloride = 0.006) to high (e.g. copper sulfate = 35)
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: Extreme heat
2. Incompatibilities: Copper dusts or mists may react with acetylene gas to form copper acetylides, which are solids that are sensitive to shock. Some copper mists may react with magnesium metal to form flammable hydrogen gas.
3. Hazardous decomposition products: None
4. Special precautions: None

• Flammability

1. Ignition temperature: Copper dusts = 700 C (1292 F)

• Warning properties

According to Grant, copper acetoarsenite, copper chloride, copper sulfate, copper carbonate and oxide, and copper metal all produce local irritant effects when in contact with the eye. The *Documentation of TLV's* also notes that copper salts on the eye may cause "conjunctivitis or even ulceration and turbidity of the cornea." Concentrations producing these effects are not given.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of copper dusts or mists on a cellulose ester membrane filter, followed by treatment with nitric acid, solution in hydrochloric acid, and atomic absorption spectrophotometric analysis. An analytical method for copper dusts or mists is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

hemochromatosis. Access of sheep to salt licks containing 5 to 9% copper sulfate caused the sudden onset of hemolytic anemia, icterus, and hemoglobinuria followed by death in a day or two; at necropsy, the liver, kidneys, and spleen showed severe degenerative changes. Workers exposed to copper dust in concentrations of 0.075 to 0.120 mg/m³ complained of mild nasal discomfort. Exposure to the dust of copper acetate produced sneezing, coughing, digestive disorders, and fever. Metal workers exposed to complex copper salts in dust form complained of metallic taste with irritation of nasal and oral mucosa; atrophic changes in the mucous membranes were noted in subjects exposed for long periods of time. On ingestion, copper salts act as irritants and cause nausea, vomiting, abdominal pain, hemorrhagic gastritis, and diarrhea. Copper salts splashed in the eye cause conjunctivitis, corneal ulceration, and turbidity, and may produce palpebral edema. Copper particles embedded in the eye result in pronounced foreign-body reaction with characteristic discoloration of ocular tissue. Allergic contact dermatitis due to copper exposure, although rare, has been reported. Greenish discoloration of the skin and hair of some copper workers has been observed. Although copper is an essential element for health, excessive amounts can produce harmful effects.

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- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch

minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with copper salts or liquids containing copper salts.

- If employees' clothing may have become contaminated with powdered copper, copper salts, or liquids containing copper salts, employees should change into uncontaminated clothing before leaving the work premises.

- Clothing contaminated with copper salts should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of copper salts from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the copper salts, the person performing the operation should be informed of copper salts's hazardous properties.

- Non-impervious clothing which becomes contaminated with copper salts should be removed promptly and not reworn until the copper salts are removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where powdered copper or dusts, mists, or liquids containing copper salts may contact the eyes.

SANITATION

- Skin that becomes contaminated with copper salts should be promptly washed or showered with soap or mild detergent and water to remove any copper salts.

- Eating and smoking should not be permitted in areas where powdered copper, copper salts, or liquids containing copper salts are handled, processed, or stored.

- Employees who handle powdered copper, copper salts, or liquids containing copper salts should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to copper dusts or mists may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining, extracting, and refining copper ore; during fabrication and manufacture of copper rod, wire, piping, and tubing for use in electrical, plumbing, and building industries; during manufacture of domestic utensils; during manufacture of alloys	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation

Liberation from production and application of fungicides, insecticides, and germicides for soil, feed, grain, textile, water and sewage treatments; during use of copper salts for paint pigments and coloring agents, electroplating baths, wood preservation, automotive emission controls, textile treatment, and organic synthesis

Controls

Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If copper dusts or mists get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

• Skin Exposure

If copper salts or liquids containing copper salts get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If copper salts or liquids containing copper salts penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of copper dusts or mists, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When powdered copper, copper salts, or liquids containing copper salts have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with copper salts or liquids containing copper salts.

- If employees' clothing may have become contaminated with powdered copper, copper salts, or liquids containing copper salts, employees should change into uncontaminated clothing before leaving the work premises.
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Liberation from production and application of fungicides, insecticides, and germicides for soil, feed, grain, textile, water and sewage treatments; during use of copper salts for paint pigments and coloring agents, electroplating baths, wood preservation, automotive emission controls, textile treatment, and organic synthesis

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know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of release until cleanup has been completed.

- If copper dusts or mists are spilled or released, the following steps should be taken:

1. Ventilate area of release.

2. Collect spilled material in the most convenient and safe manner for reclamation, or for disposal in a secured sanitary landfill. Liquid containing copper should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Copper dusts or mists and copper compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Copper as Cu," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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RESPIRATORY PROTECTION FOR COPPER DUSTS AND MISTS

Condition	Minimum Respiratory Protection* Required Above 1 mg/m ³
Particulate Concentration	
50 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2000 mg/m ³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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2000 mg/m ³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Occupational Health Guideline for Copper Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Cu/Cu₂O/CuO
- Synonyms: None
- Appearance: Finely divided particulate dispersed in air.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for copper fume is 0.1 milligram of copper fume per cubic meter of air (mg/m³) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for copper fume a Threshold Limit Value of 0.2 mg/m³.

HEALTH HAZARD INFORMATION

• Routes of exposure

Copper fume can affect the body if it is inhaled or if it comes in contact with the eyes or skin.

• Effects of overexposure

1. **Short-term Exposure:** Copper fume causes irritation of the eyes, nose, and throat, and a flu-like illness called metal fume fever. Symptoms of metal fume fever include fever, muscle aches, nausea, chills, dry throat, cough, and weakness. It may also cause a metallic or sweet taste in the mouth.

2. **Long-term Exposure:** Repeated or prolonged exposure to copper fume may cause the skin and hair to change color.

3. **Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms

and suspects that they are caused by exposure to copper fume.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to copper fume at potentially hazardous levels:

1. **Initial Medical Screening:** Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from copper fume exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of copper fume might cause exacerbation of symptoms due to its irritant properties.

—Hepatolenticular degeneration (Wilson's disease): Persons with pre-existing Wilson's disease may be more susceptible to the effects of this agent.

2. **Periodic Medical Examination:** Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

Inhalation of copper fume results in irritation of the upper respiratory tract and an influenza-like illness termed metal fume fever. Signs and symptoms of metal fume fever include chills, muscle aches, nausea, fever, dry throat, cough, weakness, and lassitude. There is usually leucocytosis, which may amount to 12,000 to 16,000/ml; recovery is usually rapid, and there are no sequelae. Most workers develop an immunity to these attacks, but it is quickly lost; attacks tend to be more severe on the first day of the work-week. Other effects from copper fume are irritation of the upper respiratory tract, metallic or sweet taste, and in some instances discoloration of the skin and hair. Exposure of workers to concentrations of 1 to 3 mg/m³ for short periods resulted in altered taste response but no nausea; levels of from 0.02 to 0.4 mg/m³ produced no complaints. Transient irritation of the eyes has followed exposure to a

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
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fine dust of oxidation products of copper produced in an electric arc.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 63.5 to 143.1
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): Not applicable
4. Vapor density (air = 1 at boiling point of copper fume): Not applicable
5. Melting point: Not applicable
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with acetylene gas may cause formation of copper acetylides that are sensitive to shock.
3. Hazardous decomposition products: None
4. Special precautions: None

• Flammability

1. Not applicable

• Warning properties

Copper fume is not known to be a significant eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of copper fume on a cellulose membrane filter, followed by treatment with nitric acid, solution in acid, and analysis with an atomic absorption spectrophotometer. An analytical method for copper fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. How-

ever, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to copper fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during construction and installation of materials fabricated from copper metal or copper alloys; during copper metal processing of castings, sheets, rods, tubing, and wire; during copper metal smelting and refining operations	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Breathing

If a person breathes in large amounts of copper fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

fine dust of oxidation products of copper produced in an electric arc.

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6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

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3. Hazardous decomposition products: None
4. Special precautions: None

• Flammability

1. Not applicable

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Copper fume is not known to be a significant eye irritant.

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SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of copper fume are inadvertently released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Copper as Cu," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR COPPER FUME

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m ³
Particulate Concentration	
1 mg/m ³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m ³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m ³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
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Occupational Health Guideline for Cyanide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all cyanides. Physical and chemical properties of two specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Potassium cyanide

- Formula: KCN
- Synonyms: None
- Appearance and odor: White solid with a faint almond odor.

Sodium cyanide

- Formula: NaCN
- Synonyms: None
- Appearance and odor: White solid with a faint almond odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for cyanide is 5 milligrams of cyanide per cubic meter of air (mg/m³) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be changed to a ceiling of 5 milligrams cyanide per cubic meter of air averaged over a 10-minute period. The NIOSH Criteria Document for Hydrogen Cyanide and Cyanide Salts should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Cyanide can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. Sufficient cyanide may be absorbed through the skin, especially if there are cuts to cause fatal poisoning.

• Effects of overexposure

1. *Short-term Exposure:* Inhalation or ingestion of cyanide salts may be rapidly fatal. Larger doses by inhalation or swallowing may cause the person to rapidly lose consciousness, stop breathing, and die. In some cases, there are convulsions. At lower levels of exposure, the earlier symptoms include weakness, headache, confusion, nausea, and vomiting. These symptoms may be followed by unconsciousness and death. Occasionally, convulsions occur. Milder forms of intoxication may result only in weakness, dizziness, headache, and nausea. The dust of cyanide salts is irritating to the eyes. In the presence of tears, it may cause the symptoms of poisoning described above. The dust of cyanide salts may produce irritation of the nose and skin. Strong solutions of cyanide salts are corrosive and may produce ulcers.

2. *Long-term Exposure:* Effects from chronic exposure to cyanide are non-specific and rare.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to cyanide.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to cyanide at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of fainting spells, such as occur in various types of cardiovascular and nervous disorders,

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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and those unusually susceptible to effects of anoxia or with anemia would be expected to be at increased risk from exposure. Examination of the cardiovascular, nervous, and upper respiratory systems, and thyroid should be stressed. The skin should be examined for evidence of chronic disorders.

—Skin disease: Cyanide is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—14" x 17" chest roentgenogram: Cyanide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Cyanide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

3. First Aid Kits: First aid kits should be readily available in workplaces where there is a potential for the release of cyanide. These kits should contain a minimum of 48 ampules, each of 0.3 ml amyl nitrate, and complete instructions for use. In addition, 2 physician's kits should be immediately available to trained medical personnel. These kits should contain the above quantity of amyl nitrate as well as sterile sodium nitrite solution (3%) and sterile sodium thiosulfate solution (25%). All of the above drugs should be replaced at least biannually to ensure their potency.

• **Summary of toxicology**

The dust of cyanide salts, a source of cyanide ion, is an asphyxiant due to an inhibitory action on metabolic enzyme systems and can be rapidly fatal. Cyanide exerts this effect because it inactivates certain enzymes by forming very stable complexes with the metal in them. Cytochrome oxidase is probably the most important of these, since it occupies a fundamental position in the respiratory process and is involved in the ultimate electron transfer to molecular oxygen. Since cytochrome oxidase is present in practically all cells that function under aerobic conditions, and since the cyanide ion diffuses easily to all parts of the body, it is capable of suddenly bringing to a halt practically all cellular respiration. In the presence of even weak acids, hydrocyanic acid (HCN) gas is liberated from cyanide salts; a few inhalations of higher concentrations of HCN may be followed by almost instantaneous collapse and cessation of respiration; 270 ppm HCN is immediately fatal to humans, 181 ppm is fatal after 10 minutes, 135 ppm after 30 minutes, and 110 ppm may be fatal in 1 hour. The ingestion by humans of 50 to 100 mg of sodium or potassium cyanide may also be fatal. At lower levels of exposure to HCN, the earliest symptoms of intoxication may include weakness, headache, confusion, and occasionally nausea and vomiting; respiratory rate and depth is usually increased initially and at later stages becomes slow and gasping; if cyanosis is present,

it usually indicates that respiration has either ceased or has been very inadequate for a few minutes. Humans tolerate 45 to 54 ppm for ½ to 1 hour without immediate or delayed effects, while 18 to 36 ppm may result in some symptoms after an exposure of several hours. Sodium cyanide dust is irritating to the eyes; in the presence of tears it may liberate HCN, which can be absorbed and cause systemic intoxication. Skin contact with dust may be irritating; strong solutions on the skin produce ulcers which are slow in healing. Cyanide is one of the few toxic materials for which an antidote exists; it functions as follows: First, amyl nitrite (inhalation) and sodium nitrite (intravenously) are administered to form methemoglobin, which binds firmly with free cyanide ions. This traps any circulating cyanide ions. The formation of 10 to 20% methemoglobin usually does not involve appreciable risk, yet provides a large amount of cyanide-binding substance. Second, sodium thiosulfate is administered intravenously to increase the rate of conversion of cyanide to the less toxic thiocyanate. Methylene blue should not be administered, because it is a poor methemoglobin former and, moreover, promotes the conversion of methemoglobin back to hemoglobin.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Potassium cyanide**

1. Molecular weight: 65.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.55
4. Vapor density (air = 1 at boiling point of potassium cyanide): Not applicable
5. Melting point: 635 C (1175 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 71.6
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium cyanide**

1. Molecular weight: 49
2. Boiling point (760 mm Hg): 1500 C (2732 F) (extrapolated)
3. Specific gravity (water = 1): 1.6
4. Vapor density (air = 1 at boiling point of sodium cyanide): Not applicable
5. Melting point: 560 C (1040 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 58
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: None. Hazardous if kept in closed containers. It may form toxic concentrations of hydrogen cyanide gas when in prolonged contact with air in a closed area.
2. Incompatibilities: Contact with strong oxidizers such as nitrates and chlorates may cause fires and

and those unusually susceptible to effects of anoxia or with anemia would be expected to be at increased risk from exposure. Examination of the cardiovascular, nervous, and upper respiratory systems, and thyroid should be stressed. The skin should be examined for evidence of chronic disorders.

—Skin disease: Cyanide is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—14" x 17" chest roentgenogram: Cyanide causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Cyanide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

3. *First Aid Kits:* First aid kits should be readily available in workplaces where there is a potential for the release of cyanide. These kits should contain a minimum of 48 ampules, each of 0.3 ml amyl nitrate, and complete instructions for use. In addition, 2 physician's kits should be immediately available to trained medical personnel. These kits should contain the above quantity of amyl nitrate as well as sterile sodium nitrite solution (3%) and sterile sodium thiosulfate solution (25%). All of the above drugs should be replaced at least biannually to ensure their potency.

• Summary of toxicology

The dust of cyanide salts, a source of cyanide ion, is an asphyxiant due to an inhibitory action on metabolic enzyme systems and can be rapidly fatal. Cyanide exerts this effect because it inactivates certain enzymes by forming very stable complexes with the metal in them. Cytochrome oxidase is probably the most important of these, since it occupies a fundamental position in the respiratory process and is involved in the ultimate electron transfer to molecular oxygen. Since cytochrome oxidase is present in practically all cells that function under aerobic conditions, and since the cyanide ion diffuses easily to all parts of the body, it is capable of suddenly bringing to a halt practically all cellular respiration. In the presence of even weak acids, hydrocyanic acid (HCN) gas is liberated from cyanide salts; a few inhalations of higher concentrations of HCN may be followed by almost instantaneous collapse and cessation of respiration; 270 ppm HCN is immediately fatal to humans, 181 ppm is fatal after 10 minutes, 135 ppm after 30 minutes, and 110 ppm may be fatal in 1 hour. The ingestion by humans of 50 to 100 mg of sodium or potassium cyanide may also be fatal. At lower levels of exposure to HCN, the earliest symptoms of intoxication may include weakness, headache, confusion, and occasionally nausea and vomiting; respiratory rate and depth is usually increased initially and at later stages becomes slow and gasping; if cyanosis is present,

it usually indicates that respiration has either ceased or has been very inadequate for a few minutes. Humans tolerate 45 to 54 ppm for ½ to 1 hour without immediate or delayed effects, while 18 to 36 ppm may result in some symptoms after an exposure of several hours. Sodium cyanide dust is irritating to the eyes; in the presence of tears it may liberate HCN, which can be absorbed and cause systemic intoxication. Skin contact with dust may be irritating; strong solutions on the skin produce ulcers which are slow in healing. Cyanide is one of the few toxic materials for which an antidote exists; it functions as follows: First, amyl nitrite (inhalation) and sodium nitrite (intravenously) are administered to form methemoglobin, which binds firmly with free cyanide ions. This traps any circulating cyanide ions. The formation of 10 to 20% methemoglobin usually does not involve appreciable risk, yet provides a large amount of cyanide-binding substance. Second, sodium thiosulfate is administered intravenously to increase the rate of conversion of cyanide to the less toxic thiocyanate. Methylene blue should not be administered, because it is a poor methemoglobin former and, moreover, promotes the conversion of methemoglobin back to hemoglobin.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data—Potassium cyanide

1. Molecular weight: 65.1
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 1.55
4. Vapor density (air = 1 at boiling point of potassium cyanide): Not applicable
5. Melting point: 635 C (1175 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 71.6
8. Evaporation rate (butyl acetate = 1): Not applicable

• Physical data—Sodium cyanide

1. Molecular weight: 49
2. Boiling point (760 mm Hg): 1500 C (2732 F) (extrapolated)
3. Specific gravity (water = 1): 1.6
4. Vapor density (air = 1 at boiling point of sodium cyanide): Not applicable
5. Melting point: 560 C (1040 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 58
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: None. Hazardous if kept in closed containers. It may form toxic concentrations of hydrogen cyanide gas when in prolonged contact with air in a closed area.
2. Incompatibilities: Contact with strong oxidizers such as nitrates and chlorates may cause fires and

explosions. Contact with acids and acid salts causes immediate formation of toxic and flammable hydrogen cyanide gas.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen cyanide and carbon monoxide) may be released when cyanide decomposes.

4. Special precautions: Cyanide may react with carbon dioxide in ordinary air to form toxic hydrogen cyanide gas.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold of sodium or potassium cyanide. HCN, however, is evolved from these substances in the presence of moisture. The Manufacturing Chemists Association states that "although HCN has a characteristic odor, its toxic action at hazardous concentrations is so rapid that it is of no value as a warning property."

2. Eye Irritation Level: Cyanide (as CN) is not known to be an eye irritant. However, according to Grant, HCN can produce eye irritation after chronic exposures.

3. Evaluation of Warning Properties: Although cyanide (as CN) has a negligible vapor pressure, in the presence of moisture HCN can be given off. HCN does not have adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of cyanide. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of cyanide with a cellulose membrane filter and an impinger containing sodium hydroxide, followed by analysis by direct potentiometry. An analytical method for cyanide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the

Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with cyanide or liquids containing cyanide.

- If employees' clothing has had any possibility of being contaminated with cyanide, employees should change into uncontaminated clothing before leaving the work premises.

- Clothing which has had any possibility of being contaminated with cyanide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of cyanide from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the cyanide, the person performing the operation should be informed of cyanide's hazardous properties.

- Where there is any possibility of exposure of an employee's body to cyanide or liquids containing cyanide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

- Non-impervious clothing which becomes contaminated with cyanide should be removed immediately and not reworn until the cyanide is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of cyanide or liquids containing cyanide contacting the eyes.

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3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen cyanide and carbon monoxide) may be released when cyanide decomposes.

4. Special precautions: Cyanide may react with carbon dioxide in ordinary air to form toxic hydrogen cyanide gas.

- **Flammability**

- 1. Not combustible

- **Warning properties**

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- Where there is any possibility of exposure of an employee's body to cyanide or liquids containing cyanide, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

- Non-impervious clothing which becomes contaminated with cyanide should be removed immediately and not reworn until the cyanide is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of cyanide or liquids containing cyanide contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to cyanide or liquids containing cyanide, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with cyanide should be immediately washed or showered with soap or mild detergent and water to remove any cyanide.
- Workers subject to skin contact with cyanide should wash with soap or mild detergent and water any areas of the body which may have contacted cyanide at the end of each work day.
- Eating and smoking should not be permitted in areas where cyanide or liquids containing cyanide are handled, processed, or stored.
- Employees who handle cyanide or liquids containing cyanide should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to cyanide may occur and control methods which may be effective in each case:

Operation	Controls
Use as fumigants and pesticides in greenhouses, ships, mills, and warehouses; use of cyanogen chloride as a warning agent in fumigant gases	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in metal treatment in nitriding, tempering, and case hardening steel; coloring of metals by chemical or electrolytic process; cleaning and coating metals; welding and cutting of heat-resistant metals; liberation during ore extraction and metal purification	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation

Use of calcium cyanamid in fertilizer on soil; during chemical synthesis for manufacture of intermediates in pharmaceuticals, dyes, vitamins, plastics, and sequestering agents; preparation of nitriles, carbamylamines, cyano fatty acids, and inorganic cyanides

Use in cellulose technology; paper manufacture; in dyeing; as cement stabilizers; use in photography as fixatives, and in blueprinting and process engraving; liberation in blast furnace gases or in handling of illuminating gas

Controls

Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

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EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If cyanide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with cyanides.

• Skin Exposure

If cyanide gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If cyanide penetrates through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

• Breathing

If a person breathes in large amounts of cyanide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When cyanide has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- Where there is any possibility that employees' eyes may be exposed to cyanide or liquids containing cyanide, an eye-wash fountain should be provided within the immediate work area for emergency use.

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- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If cyanide is spilled, the following steps should be taken:

1. Ventilate area of spill.

2. Collect spilled material in the most convenient and safe manner for reclamation, or for treatment in a cyanide disposal system.

- Waste disposal method:

After treatment as in above, cyanide may be disposed of in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Cyanide (as CN)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR CYANIDE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m ³
Particulate Concentration	
50 mg/m ³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 50 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against hydrogen cyanide and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Iron Oxide Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Fe_2O_3
- Synonyms: Ferric oxide fume
- Appearance: Red-brown fume with a metallic taste

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for iron oxide fume is 10 milligrams of iron oxide fume per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for iron oxide fume a Threshold Limit Value of $5 \text{ mg}/\text{m}^3$.

HEALTH HAZARD INFORMATION

• Routes of exposure

Iron oxide fume can affect the body if it is inhaled.

• Effects of overexposure

Repeated exposure to iron oxide fume over a period of years may cause x-ray changes of the lungs, but does not cause the exposed person to become ill.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to iron oxide fume.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to iron oxide fume at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Iron oxide fume causes an apparently benign pneumoconiosis. However, since exposure may be associated with other more toxic dust exposures, surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Iron oxide fume causes an apparently benign pneumoconiosis. However, since exposure may be associated with other more toxic dust exposures, periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing.

• Summary of toxicology

Inhalation of iron oxide fume or dust causes an apparently benign pneumoconiosis termed siderosis. Iron oxide alone does not cause fibrosis in the lungs of animals, and the same probably applies to humans. Exposures of 6 to 10 years are usually considered necessary before changes recognizable by x-ray can occur; the retained dust gives x-ray shadows that may be indistinguishable from fibrotic pneumoconiosis. Eight of 25 welders exposed chiefly to iron oxide for an average of 18.7 (range 3 to 32) years had reticulonodular shadows on chest x-rays consistent with siderosis but no reduction in pulmonary function; exposure levels ranged from 0.65 to $47 \text{ mg}/\text{m}^3$. In another study, 16 welders with an average exposure of 17.1 (range 7 to 30) years also had x-rays suggesting siderosis and spirometers which were normal; however, the static and functional compliance of the lungs was reduced; some of the welders were smokers. The welders with the lowest compliance complained of dyspnea.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Occupational Health Guideline for Iron Oxide Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Fe_2O_3
- Synonyms: Ferric oxide fume
- Appearance: Red-brown fume with a metallic taste

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for iron oxide fume is 10 milligrams of iron oxide fume per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has recommended for iron oxide fume a Threshold Limit Value of $5 \text{ mg}/\text{m}^3$.

HEALTH HAZARD INFORMATION

• Routes of exposure

Iron oxide fume can affect the body if it is inhaled.

• Effects of overexposure

Repeated exposure to iron oxide fume over a period of years may cause x-ray changes of the lungs, but does not cause the exposed person to become ill.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to iron oxide fume.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to iron oxide fume at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Iron oxide fume causes an apparently benign pneumoconiosis. However, since exposure may be associated with other more toxic dust exposures, surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Iron oxide fume causes an apparently benign pneumoconiosis. However, since exposure may be associated with other more toxic dust exposures, periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing.

• Summary of toxicology

Inhalation of iron oxide fume or dust causes an apparently benign pneumoconiosis termed siderosis. Iron oxide alone does not cause fibrosis in the lungs of animals, and the same probably applies to humans. Exposures of 6 to 10 years are usually considered necessary before changes recognizable by x-ray can occur; the retained dust gives x-ray shadows that may be indistinguishable from fibrotic pneumoconiosis. Eight of 25 welders exposed chiefly to iron oxide for an average of 18.7 (range 3 to 32) years had reticulonodular shadows on chest x-rays consistent with siderosis but no reduction in pulmonary function; exposure levels ranged from 0.65 to $47 \text{ mg}/\text{m}^3$. In another study, 16 welders with an average exposure of 17.1 (range 7 to 30) years also had x-rays suggesting siderosis and spiromograms which were normal; however, the static and functional compliance of the lungs was reduced; some of the welders were smokers. The welders with the lowest compliance complained of dyspnea.

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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 159.7
2. Boiling point (760 mm Hg): Not applicable
3. Specific gravity (water = 1): Solid = 5.24
4. Vapor density (air = 1 at boiling point of iron oxide fume): Not applicable
5. Melting point: 1566 C (2850 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact of iron oxide fume with calcium hypochlorite may cause explosions.
3. Hazardous decomposition products: None
4. Special precautions: None

- **Flammability**

1. Not combustible

- **Warning properties**

Iron oxide fume is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of iron oxide fume on a filter, followed by atomic absorption spectrophotometric analysis. An analytical method for iron oxide fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed

vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to iron oxide fume may occur and control methods which may be effective in each case:

Operation	Controls
Liberation in production of steel ingots; processing of iron ore to pig iron; heating and pouring of molten metal in foundry operations; hot rolling sheet and strip steel; fettling of castings in foundry operations; during forging of metal items containing iron/steel; pressing of metal items, grinding and polishing of glass, precious metals, stones, and gem stones	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Breathing**

If a person breathes in large amounts of iron oxide fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 159.7
 2. Boiling point (760 mm Hg): Not applicable
 3. Specific gravity (water = 1): Solid = 5.24
 4. Vapor density (air = 1 at boiling point of iron oxide fume): Not applicable
 5. Melting point: 1566 C (2850 F) (decomposes)
 6. Vapor pressure at 20 C (68 F): Zero
 7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
 8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
 1. Conditions contributing to instability: None
 2. Incompatibilities: Contact of iron oxide fume with calcium hypochlorite may cause explosions.
 3. Hazardous decomposition products: None
 4. Special precautions: None
- **Flammability**
 1. Not combustible
- **Warning properties**

Iron oxide fume is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).
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vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

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The following list includes some common operations in which exposure to iron oxide fume may occur and control methods which may be effective in each case:

Operation	Controls
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EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Breathing

If a person breathes in large amounts of iron oxide fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of iron oxide fume are inadvertently released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Iron Oxide Fume," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Harding, H. E., et al.: "Clinical, Radiographic, and Pathological Studies of the Lungs of Electric-Arc and Oxyacetylene Welders," *Lancet*, 2:394-398, 1958.
- Jones, J. G., and Warner, C. G.: "Chronic Exposure to Iron Oxide, Chromium Oxide, and Nickel Oxide

Fumes of Metal Dressers in a Steelworks," *British Journal of Industrial Medicine*, 29:169-177, 1972.

- Kleinfeld, M., et al.: "Welders' Siderosis," *Archives of Environmental Health*, 19:70-73, 1969.

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- Stanescu, D. C., et al.: "Aspects of Pulmonary Mechanics in Arc Welders' Siderosis," *British Journal of Industrial Medicine*, 24:143-147, 1967.

RESPIRATORY PROTECTION FOR IRON OXIDE FUME

Condition	Minimum Respiratory Protection* Required Above 10 mg/m ³
Particulate Concentration	
100 mg/m ³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
500 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5,000 mg/m ³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5,000 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

SPILL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of iron oxide fume are inadvertently released, ventilate the area of the release to disperse the fume.

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- American Conference of Governmental Industrial Hygienists: "Iron Oxide Fume," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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Occupational Health Guideline for Manganese

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Mn
- Synonyms: None
- Appearance: Gray solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for manganese is a ceiling level of 5 milligrams of manganese per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

Manganese can affect the body if it is inhaled. Manganese can also affect the body if it is swallowed.

• Effects of overexposure

1. *Short-term Exposure:* Inhalation of fumes with high concentrations of manganese and its oxides may bring about "metal fume fever." Symptoms of metal fume fever are chills and fever, upset stomach, vomiting, dryness of the throat, cough, weakness, and aching of the head and body. Symptoms often occur several hours after exposure to fumes and usually last for only a day.
2. *Long-term Exposure:* Prolonged or repeated exposure to manganese may affect the nervous system with difficulty in walking and balancing, weakness or cramps in the legs, hoarseness of the voice, trouble with memory and judgment, unstable emotions or unusual irritability. If high exposure continues, a person may have poor coordination, difficulty in speaking clearly, or shaking or tremor of the arms or legs. A person may

also have hallucinations or uncontrollable laughter or crying. The respiratory system may be affected by a condition known as "manganese pneumonia," which may result in symptoms and signs of coughing, fever, chills, general aching of the body, chest pain, and other common signs of pneumonia.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to manganese.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to manganese at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of alcoholism, psychiatric, neurologic, or pulmonary diseases or liver dysfunction would be expected to be at increased risk from exposure. Examination of the respiratory tract, hemopoietic system, and kidneys should be stressed.

—14" x 17" chest roentgenogram: Manganese causes pneumonitis or metal fume fever. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Manganese is reported to cause decreased pulmonary function. Periodic surveillance is indicated.

—A complete blood count: Manganese has been reported to cause blood changes. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Urinalysis: Since kidney damage has been observed in humans exposed to manganese, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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also have hallucinations or uncontrollable laughter or crying. The respiratory system may be affected by a condition known as "manganese pneumonia," which may result in symptoms and signs of coughing, fever, chills, general aching of the body, chest pain, and other common signs of pneumonia.

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sediment. Determination of manganese level in urine may be helpful in assessing exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

• **Summary of toxicology**

Inhalation of manganese dust or fume primarily affects the central nervous system; high concentrations cause the influenza-like illness termed manganese pneumonitis. Manganese acts either as a direct neurotoxin, or it adversely affects certain neuroenzymes. Manganese fume causes a disease quite similar to Parkinsonism after 6 months to 2 years of exposure. Initially there is headache; asthenia; restless sleep or somnolence; change in personality with psychomotor instability associated with restlessness, irritability, and a tendency to either cry or laugh inappropriately. This is followed by an intermediate phase with visual hallucinations, double vision; impaired hearing; uncontrollable impulses; mental confusion; euphoria; and normal reaction to painful stimuli. In the advanced phase, the subject exhibits possible anemia; excessive salivation; disorders of the basal ganglia of Parkinsonian type, such as mask-like facies, muscle weakness, muscle rigidity, tremor of the upper extremities and head, and impaired gait. High concentrations of manganese dust produce fever and chills similar to mental fume fever. During human exposure to manganese fume there is dryness and irritation of the throat, a sweet or metallic taste followed by substernal tightness, constriction in the chest, and a dry cough. Several hours following exposure the subject develops chills, lassitude, malaise, fatigue, frontal headache, low back pain, muscle cramps, and occasionally blurred vision, nausea, and vomiting. Physical examination reveals fever, perspiration, dyspnea, rales throughout the chest, and tachycardia; in some instances there has been a reversible reduction in pulmonary vital capacity. Leukopenia has been reported in 4 out of 16 cases of manganese poisoning, although there is no convincing evidence that any changes in the blood should be regarded as specific or diagnostic of manganese poisoning.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 54.94
2. Boiling point (760 mm Hg): 2097 C (3806 F)
3. Specific gravity (water = 1): 7.2
4. Vapor density (air = 1 at boiling point of manganese): Data not available
5. Melting point: 1245 C (2273 F)
6. Vapor pressure at 1227 C (2240 F): 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Not pertinent
8. Evaporation rate (butyl acetate = 1): Not pertinent

2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Data not available
4. Extinguishant: Data not available

• **Warning properties**

Grant states that "local contact of manganese with the cornea does not appear to be a problem industrially."

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of manganese. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of manganese in a filter, followed by atomic absorption spectrophotometric analysis. An analytical method for manganese is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

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COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to manganese may occur and control methods which may be effective in each case:

sediment. Determination of manganese level in urine may be helpful in assessing exposure.

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• **Summary of toxicology**

Inhalation of manganese dust or fume primarily affects the central nervous system; high concentrations cause the influenza-like illness termed manganese pneumonitis. Manganese acts either as a direct neurotoxin, or it adversely affects certain neuroenzymes. Manganese fume causes a disease quite similar to Parkinsonism after 6 months to 2 years of exposure. Initially there is headache; asthenia; restless sleep or somnolence; change in personality with psychomotor instability associated with restlessness, irritability, and a tendency to either cry or laugh inappropriately. This is followed by an intermediate phase with visual hallucinations, double vision; impaired hearing; uncontrollable impulses; mental confusion; euphoria; and normal reaction to painful stimuli. In the advanced phase, the subject exhibits possible anemia; excessive salivation; disorders of the basal ganglia of Parkinsonian type, such as mask-like facies, muscle weakness, muscle rigidity, tremor of the upper extremities and head, and impaired gait. High concentrations of manganese dust produce fever and chills similar to mental fume fever. During human exposure to manganese fume there is dryness and irritation of the throat, a sweet or metallic taste followed by substernal tightness, constriction in the chest, and a dry cough. Several hours following exposure the subject develops chills, lassitude, malaise, fatigue, frontal headache, low back pain, muscle cramps, and occasionally blurred vision, nausea, and vomiting. Physical examination reveals fever, perspiration, dyspnea, rales throughout the chest, and tachycardia; in some instances there has been a reversible reduction in pulmonary vital capacity. Leukopenia has been reported in 4 out of 16 cases of manganese poisoning, although there is no convincing evidence that any changes in the blood should be regarded as specific or diagnostic of manganese poisoning.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 54.94
2. Boiling point (760 mm Hg): 2097 C (3806 F)
3. Specific gravity (water = 1): 7.2
4. Vapor density (air = 1 at boiling point of manganese): Data not available
5. Melting point: 1245 C (2273 F)
6. Vapor pressure at 1227 C (2240 F): 1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Not pertinent
8. Evaporation rate (butyl acetate = 1): Not pertinent

2 Manganese

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Data not available

• **Warning properties**

Grant states that "local contact of manganese with the cornea does not appear to be a problem industrially."

MONITORING AND MEASUREMENT PROCEDURES

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of manganese. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of manganese in a filter, followed by atomic absorption spectrophotometric analysis. An analytical method for manganese is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to manganese may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during welding operations	Local exhaust ventilation; respiratory protective devices; dilution ventilation
Liberation during casting of molten ferro-manganese	Local exhaust ventilation
Liberating during bagging of manganese ore	Local exhaust ventilation; respiratory protective devices and dust suppression with water
Liberation during mixing and pressing of dry battery depolarization	Local exhaust ventilation
Liberation during grinding of ore containing manganese	Local exhaust ventilation; respiratory protective devices and dust suppression with water
Liberation during arc burning of manganese-hardened steel in repair and manufacture programs	Local exhaust ventilation; respiratory protective devices; dilution ventilation
Liberation from top of submerged arc electric furnace	General dilution ventilation and process enclosure, if possible
Liberation of dust during ore extraction	General dilution ventilation; respiratory protective devices
Liberation during metal finishing operations of high manganese steel	Local exhaust ventilation; respiratory protective equipment
Liberation of dust during crushing of ferro-manganese metal prior to shipment; during dumping, weighing, and mixing operations in ceramics and glass manufacture for pigmentation and coloration purposes	Local exhaust ventilation; respiratory protective equipment
Liberation from formulation of proprietary mixtures for paint and varnish manufacture	Local exhaust ventilation; respiratory protective equipment

Operation	Controls
Liberation of dioxide and sulfate during manufacture and application of fertilizers	Local exhaust ventilation
Liberation of dust during manufacture of manganese soap and wood preservatives; manufacture of safety matches, signal flares, fire-works, and strikers; during mixing and kiln operations of brick manufacture	Local exhaust ventilation
Liberation of dusts during manufacture and utilization of oxidation catalysts, such as hopcalite, manganese acetate, and naphthenate	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Breathing

If a person breathes in large amounts of manganese, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When manganese has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If manganese is spilled, the following steps should be taken:

1. Remove all ignition sources.

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SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If manganese is spilled, the following steps should be taken:

1. Remove all ignition sources.

2. Ventilate area of spill.

2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

• Waste disposal methods:

Manganese may be disposed of:

1. By making packages of manganese in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

2. By dissolving manganese in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

ADDITIONAL INFORMATION

To find additional information on manganese, look up manganese in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Manganese," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Manganese," *Hygienic Guide Series*, Detroit, Michigan, 1962.

• American National Standard Acceptable Concentrations - Manganese: ANSI-Z37.6-1948, American National Standards Institute, Inc., New York, 1948.

• Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.

• Dow Chemical Company: *Material Safety Data Sheet - Manganese*, Midland, Michigan, 1975.

• Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.

• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

• *Hygienic Information Guide No. 29 - Manganese*, Commonwealth of Pennsylvania, Department of Environmental Resources, Bureau of Occupational Health, 1973.

• International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Penalver, R.: "Manganese Poisoning," *Industrial Medicine and Surgery*, 24:1-7, 1955.

• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

• Smyth, L. T., et al.: "Clinical Manganism and Exposure to Manganese in the Production and Processing of Ferromanganese Alloy," *Journal of Occupational Medicine*, 15:101-109, 1973.

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RESPIRATORY PROTECTION FOR MANGANESE

Condition	Minimum Respiratory Protection* Required Above 5 mg/m ³
Dust or Mist Concentration	
25 mg/m ³ or less	Any dust and mist respirator, except single-use respirators.
50 mg/m ³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
Dust, Mist, or Fume Concentration	
50 mg/m ³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m ³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
10,000 mg/m ³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 10,000 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Inorganic Mercury

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: Hg
- Synonyms: Quicksilver
- Appearance and odor: Silvery, mobile, odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for mercury is a ceiling level of 0.1 milligram of mercury per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 0.05 mg/m^3 averaged over an eight-hour work shift. The NIOSH Criteria Document for Inorganic Mercury should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Mercury can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It may enter the body through the skin.

• Effects of overexposure

1. *Short-term Exposure:* Inhaled mercury vapor may cause headaches, cough, chest pains, chest tightness, and difficulty in breathing. It may also cause chemical pneumonitis. In addition, it may cause soreness of the mouth, loss of teeth, nausea, and diarrhea. Liquid mercury may irritate the skin.

2. *Long-term Exposure:* Repeated or prolonged exposure to mercury liquid or vapor causes effects which develop gradually. The first effects to occur are often

fine shaking of the hands, eyelids, lips, tongue, or jaw. Other effects are allergic skin rash, headache, sores in the mouth, sore and swollen gums, loose teeth, insomnia, excess salivation, personality change, irritability, indecision, loss of memory, and intellectual deterioration.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to mercury.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to mercury at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of allergies or known sensitization to mercury, chronic respiratory disease, nervous system disorders, or kidney disease would be expected to be at increased risk from exposure. Examination for any signs or symptoms of unacceptable mercury absorption such as weight loss, insomnia, tremors, personality changes, or other evidence of central nervous system involvement, as well as evidence of kidney damage, should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in humans exposed to mercury, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. Determination of mercury level in urine may be helpful in assessing extent of absorption.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
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- **Summary of toxicology**

Acute exposure to mercury at high levels causes severe respiratory irritation, digestive disturbances, and marked renal damage; chronic mercurialism, the form of intoxication most frequently caused by occupational exposure, is characterized by neurologic and psychic disturbances, anorexia, weight loss, and stomatitis. Skin absorption of inorganic mercury probably adds to the toxic effects of vapor inhalation. Intraperitoneal injection of metallic mercury in rats has produced sarcomas. Exposure of humans to mercury vapor in concentrations of 1.2 to 8.5 mg/m³ causes cough, chest pain and dyspnea, leading to bronchitis and pneumonitis. Metallic mercury readily vaporizes at room temperature, and the vapor has no warning properties. At low levels, the onset of symptoms resulting from chronic exposure is insidious; fine tremors of the hands, eyelids, lips and tongue are often the presenting complaint. Coarse jerky movements and incoordination may interfere with the fine movements considered necessary for writing and eating. Psychic disturbances such as insomnia, irritability, and indecision occur; headache, excessive fatigue, anorexia, digestive disturbances, and weight loss are common; stomatitis with excessive salivation is sometimes severe; muscle weakness has been reported. Proteinuria may occur, but is relatively infrequent. Mercury has been reported to be capable of causing sensitization dermatitis. Examination of urine for mercury may be of value. There is no "critical" level of mercury in urine above or below which poisoning cannot be seen. Various observers have suggested from 0.1 to 0.5 mg of Hg/l of urine as having clinical significance. Mercury, particularly organic forms, is known to adversely affect the fetus if the mother is exposed during pregnancy.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 200.6
2. Boiling point (760 mm Hg): 357 C (674 F)
3. Specific gravity (water = 1): 13.5
4. Vapor density (air = 1 at boiling point of mercury): Not applicable
5. Melting point: -39 C (-38 F)
6. Vapor pressure at 20 C (68 F): 0.0012 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.002
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with acetylene, acetylene products, or ammonia gases may form solid products that are sensitive to shock and which can initiate fires of combustible materials.
3. Hazardous decomposition products: None
4. Special precautions: Mercury can attack copper and copper alloy materials.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Mercury is odorless.
2. Eye Irritation Level: Grant states that "when mercury metal droplets are in the epithelium, rather than the corneal stroma or anterior chamber, they are extruded rapidly with little reaction, as was reported in a patient who was sprayed forcefully with metallic mercury and was observed to have many fine silvery globules beneath the epithelium of the cornea

"Mercury metal in contact with the conjunctiva has been shown in rabbits to be absorbed and ultimately to be detectable in the urine. While in contact with the conjunctiva, metallic mercury produced no clinical signs of conjunctivitis, but histologically an inflammatory reaction has been demonstrable. External contact with mercury vapor has repeatedly been observed to induce a characteristic discoloration of the crystalline lens (mercurialentis)." Mercurialentis also is caused by systemic poisoning "from absorption of mercury vapor through the respiratory tract, the skin, and the gastrointestinal tract."

For the purposes of this guideline, mercury is not treated as an eye irritant.

3. Evaluation of Warning Properties: Mercury has no warning properties, according to the *Hygienic Guide*.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of mercury. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of mercury with a three-section solid phase sampler, followed by analysis with an atomic absorption spectrophotometer. An analytical method for mercury is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

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2. Incompatibilities: Contact with acetylene, acetylene products, or ammonia gases may form solid products that are sensitive to shock and which can initiate fires of combustible materials.
3. Hazardous decomposition products: None
4. Special precautions: Mercury can attack copper and copper alloy materials.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Mercury is odorless.
2. Eye Irritation Level: Grant states that "when mercury metal droplets are in the epithelium, rather than the corneal stroma or anterior chamber, they are extruded rapidly with little reaction, as was reported in a patient who was sprayed forcefully with metallic mercury and was observed to have many fine silvery globules beneath the epithelium of the cornea

"Mercury metal in contact with the conjunctiva has been shown in rabbits to be absorbed and ultimately to be detectable in the urine. While in contact with the conjunctiva, metallic mercury produced no clinical signs of conjunctivitis, but histologically an inflammatory reaction has been demonstrable. External contact with mercury vapor has repeatedly been observed to induce a characteristic discoloration of the crystalline lens (mercurialentis)." Mercurialentis also is caused by systemic poisoning "from absorption of mercury vapor through the respiratory tract, the skin, and the gastrointestinal tract."

For the purposes of this guideline, mercury is not treated as an eye irritant.

3. Evaluation of Warning Properties: Mercury has no warning properties, according to the *Hygienic Guide*.

MONITORING AND MEASUREMENT PROCEDURES

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of mercury. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of mercury with a three-section solid phase sampler, followed by analysis with an atomic absorption spectrophotometer. An analytical method for mercury is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may

be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid mercury.
- If employees' clothing may have become contaminated with mercury, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with mercury should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of mercury from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the mercury, the person performing the operation should be informed of mercury's hazardous properties.
- Non-impervious clothing which becomes contaminated with mercury should be removed promptly and not reworn until the mercury is removed from the clothing.

SANITATION

- Workers subject to skin contact with liquid mercury should wash with soap or mild detergent and water any areas of the body which may have contacted mercury at the end of each work day.
- Skin that becomes contaminated with mercury should be promptly washed or showered with soap or mild detergent and water to remove any mercury.
- Eating and smoking should not be permitted in areas where mercury is handled, processed, or stored.
- Employees who handle mercury should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to mercury may occur and control methods which may be effective in each case:

Operation

Use as a liquid cathode in electrolytic production of chlorine and caustic soda from brine

Use during manufacture and repair of industrial and medical apparatus; use during manufacture of inorganic and organic compounds for use as pesticides, antiseptics, germicides, and skin preparations, and miscellaneous applications as chemical intermediates, preservatives, and pigments

Use in preparation of amalgams for use in tooth restorations, chemical processing, and molding operations; use during manufacture of mildew-proof paints and marine antifouling agents

Use in manufacture of organic mercurials; use in manufacture of batteries, lamps, and power tubes; manufacture of tungsten-molybdenum wire and rods; use in manufacture of inorganic salts for use as catalysts in production of urethanes, vinyl chloride monomers, anthraquinone derivatives, and other miscellaneous chemicals

Controls

General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping

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Operation	Controls
Use as a chemical intermediate and in the manufacture of felt; as a flotation agent in manufacture of bowling balls; use as a laboratory reagent or as a working fluid in instruments	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping
Use as a conductor during construction and maintenance of military and nuclear power systems, in mercury-stem boilers, and in air-rectifiers	General dilution ventilation; personal protective equipment; meticulous housekeeping
Liberation during roasting and smelting operations	General dilution ventilation; local exhaust ventilation
Use in manufacture of explosives; in preparation of amalgams for use in artificial jewelry	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment; meticulous housekeeping
Use in manufacture of compounds for pulp and paper industry as controls for biological growths	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Liberation during mining and subsequent refining of ore containing cinnabar	General dilution ventilation; personal protective equipment; meticulous housekeeping

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If liquid mercury gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If liquid mercury gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid mercury penetrates through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of mercury, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When large quantities of mercury have been swallowed or mercury has been swallowed repeatedly and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If mercury is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material for reclamation using commercially available mercury vapor depressants or specialized vacuum cleaners.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Mercury as Hg," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Mercury and Its Inorganic Compounds," *Hygienic Guide Series*, Detroit, Michigan, 1966.
- American National Standard Acceptable Concentrations - Mercury: ANSI-Z37.8-1972, American National Standards Institute, Inc., New York, 1972.
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- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Vostal, J. J., and Clarkson, T. W.: "Mercury as an Environmental Hazard," *Journal of Occupational Medicine*, 15:649-656, 1973.
- "Working with Mercury in Industry," U.S. Department of Health, Education, and Welfare Pamphlet, U.S. Government Printing Office, Washington, D.C., 1973.

RESPIRATORY PROTECTION FOR INORGANIC MERCURY

Condition	Minimum Respiratory Protection* Required Above 0.1 mg/m ³
Particulate or Vapor Concentration	
1 mg/m ³ or less	Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m ³ or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
28 mg/m ³ or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 28 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against mercury. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Nickel Metal and Soluble Nickel Compounds

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all soluble nickel compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Nickel, metallic

- Formula: Ni
- Synonyms: Nickel catalyst; Raney nickel
- Appearance and odor: Silvery gray, metallic (or darker), odorless powder.

Nickel nitrate hexahydrate

- Formula: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- Synonyms: None
- Appearance and odor: Green, odorless solid.

Nickel sulfate hexahydrate

- Formula: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
- Synonyms: None
- Appearance and odor: Green, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nickel metal and soluble nickel compounds is 1 milligram of nickel metal

and soluble nickel compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit for nickel be reduced to $0.015 \text{ mg}/\text{m}^3$ averaged over a work shift of up to 10 hours per day, 40 hours per week, and that nickel be regulated as an occupational carcinogen. The NIOSH Criteria Document for Inorganic Nickel and the Special Occupational Hazard Review for Nickel Carbonyl should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Metallic nickel or soluble nickel compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

• Effects of overexposure

Nickel fumes are respiratory irritants and may cause pneumonitis. Skin contact may cause an allergic skin rash. Nickel and its compounds have been reported to cause cancer of the lungs and sinuses. Nickel itself is not very toxic if swallowed, but its soluble salts are quite toxic and, if swallowed, may cause giddiness and nausea. Exposure to nickel carbonyl (by inhalation or skin absorption) may cause both initial and delayed symptoms. Initial symptoms include headache, dizziness, shortness of breath, and vomiting. These symptoms generally disappear when the worker is exposed to fresh air. The delayed symptoms may develop 12 to 36 hours after exposure. The shortness of breath returns, a blue color of the skin may appear, and a fever may develop. The exposed person may become delirious. In some cases the symptoms may run together. Death may occur.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nickel metal and soluble nickel compounds.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
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- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nickel metal and soluble nickel compounds at potentially hazardous levels:

- 1. **Initial Medical Examination:**

- A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to nickel metal and soluble nickel compounds would be expected to be at increased risk from exposure. Examination of the nasal cavities and lungs should be stressed. The skin should be examined for evidence of chronic disorders.

- 14" x 17" chest roentgenogram: Nickel metal and soluble nickel compounds cause human lung damage and cancer of the lung. Surveillance of the lungs is indicated.

- FVC and FEV (1 sec): Nickel metal and soluble nickel compounds are respiratory irritants. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

- Skin disease: Nickel metal and soluble compounds are defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

- 2. **Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Metallic nickel and certain soluble nickel compounds as dust or fume cause sensitization dermatitis and probably produce cancer of the paranasal sinuses and the lung; nickel fume in high concentrations is a respiratory irritant. Severe but transient pneumonitis in two workers resulted from exposure to nickel fume; in one case, exposure was for 6 hours, and post-incident sampling suggested a nickel concentration of 0.26 mg/m³. "Nickel itch" is a dermatitis resulting from sensitization to nickel; the first symptom is usually itching, which occurs up to 7 days before skin eruption appears. The primary skin eruption is erythematous, or follicular; it may be followed by superficial discrete ulcers, which discharge and become crusted, or by eczema; in the chronic stages, pigmented or depigmented plaques may be formed. Nickel sensitivity, once acquired, is apparently not lost; recovery from the dermatitis usually occurs within 7 days of cessation of exposure, but may take several weeks. A worker who had developed cutaneous sensitization also developed apparent asthma from inhalation of nickel sulfate; immunologic studies showed circulating antibodies to the salt, and controlled exposure to a solution of nickel sulfate resulted in decreased pulmonary function and progressive dyspnea; the possibility of developing hypersensitivity pneumonitis could not be excluded. In animals, finely

divided metallic nickel was carcinogenic when introduced into the pleural cavity, muscle tissue, and subcutaneous tissues; rats and guinea pigs exposed to a concentration of 15 mg/m³ of powdered metallic nickel developed malignant pulmonary neoplasms. Several epidemiologic studies have shown an increased incidence of cancer of the paranasal sinuses and lungs among workers in nickel refineries and factories; suspicion of carcinogenicity has been focused primarily on respirable particles of nickel, nickel subsulfide, nickel oxide, and on nickel carbonyl vapor. Many of the studies also included exposures to other suspected carcinogens.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Nickel, metallic**

1. Molecular weight: 58.7
2. Boiling point (760 mm Hg): 2730 C (4946 F)
3. Specific gravity (water = 1): 8.9
4. Vapor density (air = 1 at boiling point of metallic nickel): Not applicable
5. Melting point: 1453 C (2648 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Nickel nitrate hexahydrate**

1. Molecular weight: 290.8
2. Boiling point (760 mm Hg): 137 C (278 F) (loses water)
3. Specific gravity (water = 1): 2.05
4. Vapor density (air = 1 at boiling point of nickel nitrate hexahydrate): Not applicable
5. Melting point: 57 C (135 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 60

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Nickel sulfate hexahydrate**

1. Molecular weight: 262.8
2. Boiling point (760 mm Hg): 103 C (217 F) (loses water)
3. Specific gravity (water = 1): 2.07
4. Vapor density (air = 1 at boiling point of nickel sulfate hexahydrate): Not applicable
5. Melting point: 53 C (127 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 40

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat (nickel only)
2. Incompatibilities: Contact of nickel with strong acids may form flammable and explosive hydrogen gas.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nickel metal and soluble nickel compounds at potentially hazardous levels:

1. **Initial Medical Examination:**

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to nickel metal and soluble nickel compounds would be expected to be at increased risk from exposure. Examination of the nasal cavities and lungs should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Nickel metal and soluble nickel compounds cause human lung damage and cancer of the lung. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nickel metal and soluble nickel compounds are respiratory irritants. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Skin disease: Nickel metal and soluble compounds are defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

2. **Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

Metallic nickel and certain soluble nickel compounds as dust or fume cause sensitization dermatitis and probably produce cancer of the paranasal sinuses and the lung; nickel fume in high concentrations is a respiratory irritant. Severe but transient pneumonitis in two workers resulted from exposure to nickel fume; in one case, exposure was for 6 hours, and post-incident sampling suggested a nickel concentration of 0.26 mg/m³. "Nickel itch" is a dermatitis resulting from sensitization to nickel; the first symptom is usually itching, which occurs up to 7 days before skin eruption appears. The primary skin eruption is erythematous, or follicular; it may be followed by superficial discrete ulcers, which discharge and become crusted, or by eczema; in the chronic stages, pigmented or depigmented plaques may be formed. Nickel sensitivity, once acquired, is apparently not lost; recovery from the dermatitis usually occurs within 7 days of cessation of exposure, but may take several weeks. A worker who had developed cutaneous sensitization also developed apparent asthma from inhalation of nickel sulfate; immunologic studies showed circulating antibodies to the salt, and controlled exposure to a solution of nickel sulfate resulted in decreased pulmonary function and progressive dyspnea; the possibility of developing hypersensitivity pneumonitis could not be excluded. In animals, finely

divided metallic nickel was carcinogenic when introduced into the pleural cavity, muscle tissue, and subcutaneous tissues; rats and guinea pigs exposed to a concentration of 15 mg/m³ of powdered metallic nickel developed malignant pulmonary neoplasms. Several epidemiologic studies have shown an increased incidence of cancer of the paranasal sinuses and lungs among workers in nickel refineries and factories; suspicion of carcinogenicity has been focused primarily on respirable particles of nickel, nickel subsulfide, nickel oxide, and on nickel carbonyl vapor. Many of the studies also included exposures to other suspected carcinogens.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Nickel, metallic**

1. Molecular weight: 58.7
2. Boiling point (760 mm Hg): 2730 C (4946 F)
3. Specific gravity (water = 1): 8.9
4. Vapor density (air = 1 at boiling point of metallic nickel): Not applicable
5. Melting point: 1453 C (2648 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Nickel nitrate hexahydrate**

1. Molecular weight: 290.8
2. Boiling point (760 mm Hg): 137 C (278 F) (loses water)
3. Specific gravity (water = 1): 2.05
4. Vapor density (air = 1 at boiling point of nickel nitrate hexahydrate): Not applicable
5. Melting point: 57 C (135 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 60
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Nickel sulfate hexahydrate**

1. Molecular weight: 262.8
2. Boiling point (760 mm Hg): 103 C (217 F) (loses water)
3. Specific gravity (water = 1): 2.07
4. Vapor density (air = 1 at boiling point of nickel sulfate hexahydrate): Not applicable
5. Melting point: 53 C (127 F)
6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 40
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat (nickel only)
2. Incompatibilities: Contact of nickel with strong acids may form flammable and explosive hydrogen gas.

Contact with sulfur may cause evolution of heat. Contact of nickel nitrate with wood and other combustibles may cause fire.

3. Hazardous decomposition products: Toxic gases and vapors (such as nickel carbonyl and oxides of nitrogen) may be released in a fire involving nickel or in the decomposition of nickel compounds.

4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable

2. Minimum ignition temperature: Not available

3. Minimum explosive concentration: Not available, but nickel sponge catalyst may ignite spontaneously in air.

4. Extinguishant: Dry powder, dry sand, dry dolomite, dry graphite

- **Warning properties**

Grant states that "workers employed in nickel plating involving nickel sulfate, sulfuric acid, and chlorine are said to have developed conjunctivitis and epiphora when ventilation was poor." Since, according to Grant, "both sulfuric acid mist and chlorine gas are known to cause burning and stinging of the eyes," and since the *AIHA Hygienic Guide* states that eye contact "does not present any problem peculiar to nickel," nickel metal and soluble compounds are not treated as eye irritants.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection on a cellulose membrane filter followed by treatment with nitric and perchloric acids, solution in nitric acid, and analysis with an atomic absorption spectrophotometer. An analytical method for nickel metal and soluble nickel compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1), number PB 258 433).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not

technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with powdered metallic nickel or solids or liquids containing soluble nickel compounds.

- If employees' clothing may have become contaminated with powdered metallic nickel or solid soluble nickel compounds, employees should change into uncontaminated clothing before leaving the work premises.

- Clothing contaminated with metallic nickel or soluble nickel compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of metallic nickel or soluble nickel compounds from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the metallic nickel or soluble nickel compounds, the person performing the operation should be informed of these substances's hazardous properties.

- Non-impervious clothing which becomes contaminated with metallic nickel or soluble nickel compounds should be removed promptly and not reworn until the metallic nickel or soluble nickel compounds are removed from the clothing.

SANITATION

- Skin that becomes contaminated with metallic nickel or soluble nickel compounds should be promptly washed or showered with soap or mild detergent and water to remove any metallic nickel or soluble nickel compounds.

- Eating and smoking should not be permitted in areas where solids or liquids containing soluble nickel compounds are handled, processed, or stored.

- Employees who handle powdered metallic nickel or solids or liquids containing soluble nickel compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

- Areas in which exposure to nickel metal and soluble nickel compounds may occur should be identified by

Contact with sulfur may cause evolution of heat. Contact of nickel nitrate with wood and other combustibles may cause fire.

3. Hazardous decomposition products: Toxic gases and vapors (such as nickel carbonyl and oxides of nitrogen) may be released in a fire involving nickel or in the decomposition of nickel compounds.

4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable

2. Minimum ignition temperature: Not available

3. Minimum explosive concentration: Not available, but nickel sponge catalyst may ignite spontaneously in air.

4. Extinguishant: Dry powder, dry sand, dry dolomite, dry graphite

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- **Method**

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- If employees' clothing may have become contaminated with powdered metallic nickel or solid soluble nickel compounds, employees should change into uncontaminated clothing before leaving the work premises.

- Clothing contaminated with metallic nickel or soluble nickel compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of metallic nickel or soluble nickel compounds from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the metallic nickel or soluble nickel compounds, the person performing the operation should be informed of these substances' hazardous properties.

- Non-impervious clothing which becomes contaminated with metallic nickel or soluble nickel compounds should be removed promptly and not reworn until the metallic nickel or soluble nickel compounds are removed from the clothing.

SANITATION

- Skin that becomes contaminated with metallic nickel or soluble nickel compounds should be promptly washed or showered with soap or mild detergent and water to remove any metallic nickel or soluble nickel compounds.

- Eating and smoking should not be permitted in areas where solids or liquids containing soluble nickel compounds are handled, processed, or stored.

- Employees who handle powdered metallic nickel or solids or liquids containing soluble nickel compounds should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

- Areas in which exposure to nickel metal and soluble nickel compounds may occur should be identified by

signs or appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nickel metal and soluble nickel compounds may occur and control methods which may be effective in each case:

Operation	Controls
Use during manufacture and fabricating of more than 3000 alloys; use in electronic tube parts, coins heavy machinery, tools, instrument parts, magnets, food and chemical processing equipment, flatware, jet engines, automotive parts, zippers, nickel anodes, surgical and dental instruments, and cooking utensils (they aid in corrosion- and heat-resistance, enhance ductibility, and increase thermal conductivity)	General dilution ventilation; local exhaust ventilation; personal protective equipment
Liberation during processing and refining of ore	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of nickel-iron alloys, and non-ferrous-nickel alloys	Local exhaust ventilation; general dilution ventilation
Use during fabrication of nickel-plated materials	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in chemical synthesis as starting material of complex compounds; use as catalysts in hydrogenation of fats/oils	General dilution ventilation
Use in textile industry in dyeing and printing; and in ceramic industry in coloring	General dilution ventilation; local exhaust ventilation

Operation

Use of metal and salts during electroplating and electroless plating

Use in manufacture of nickel-iron alloys and non-ferrous-nickel alloys

Controls

General dilution ventilation; local exhaust ventilation; personal protective equipment

Local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Skin Exposure

If solids or liquids containing soluble nickel compounds get on the skin, immediately flush the contaminated skin with water. If solids or liquids containing soluble nickel compounds penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. Metallic nickel should be removed from the skin by washing with soap or mild detergent and water.

• Breathing

If a person breathes in large amounts of metallic nickel or soluble nickel compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible. If any nickel carbonyl has been inhaled, get medical attention promptly.

• Swallowing

When metallic nickel or solids or liquids containing soluble nickel compounds have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If nickel metal and soluble nickel compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.

signs or appropriate means, and access to these areas should be limited to authorized persons.

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The following list includes some common operations in which exposure to nickel metal and soluble nickel compounds may occur and control methods which may be effective in each case:

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Liberation during processing and refining of ore	General dilution ventilation; local exhaust ventilation; personal protective equipment
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Use during fabrication of nickel-plated materials	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use in chemical synthesis as starting material of complex compounds; use as catalysts in hydrogenation of fats/oils	General dilution ventilation
Use in textile industry in dyeing and printing; and in ceramic industry in coloring	General dilution ventilation; local exhaust ventilation

Operation

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SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If nickel metal and soluble nickel compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.

2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing nickel should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Nickel metal and soluble nickel compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Nickel Ni," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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• National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *NIOSH Special Occupational Hazard Review for Nickel Carbonyl*, HEW Publication No. (NIOSH) 77-184, U.S. Government Printing Office, Washington, D.C., 1977.

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* SPECIAL NOTE

Nickel metal and soluble nickel compounds appear on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding their carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 11, 1976.

2. Collect spilled material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Liquid containing nickel should be absorbed in vermiculite, dry sand, earth, or a similar material.

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RESPIRATORY PROTECTION FOR NICKEL METAL AND SOLUBLE COMPOUNDS

Condition	Minimum Respiratory Protection* Required Above 1 mg/m ³
Dust or Mist Concentration	
5 mg/m ³ or less	Any dust and mist respirator.
10 mg/m ³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator.
50 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 mg/m ³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
2000 mg/m ³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 2000 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Greater than 2000 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
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Condition	Minimum Respiratory Protection* Required Above 1 mg/m ³
Dust, Mist, or Fume Concentration	
10 mg/m ³ or less	Any fume respirator or high efficiency particulate respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
50 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
1000 mg/m ³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
2000 mg/m ³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
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Occupational Health Guideline for Selenium and Its Inorganic Compounds (as Selenium)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all selenium and its inorganic compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Selenium

- Formula: Se
- Synonyms: Selenium, metallic; selenium, elemental
- Appearance and odor: Black, gray, or red odorless solid.

Sodium selenite

- Formula: Na_2SeO_3
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Sodium selenate

- Formula: Na_2SeO_4
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Selenium dioxide

- Formula: SeO_2
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Selenium oxychloride

- Formula: SeOCl_2
- Synonyms: None
- Appearance: Colorless to yellow liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for selenium and its inorganic compounds is 0.2 milligram of selenium and its inorganic compounds (as selenium) per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

• Routes of exposure

Selenium, sodium selenite, sodium selenate, or selenium dioxide can affect the body if they are inhaled, if they come in contact with the eyes or skin, or if they are swallowed. Selenium oxychloride and selenium dioxide may enter the body through the skin.

• Effects of overexposure

1. *Short-term Exposure:* Inhalation of large quantities of selenium dioxide or selenium oxychloride may cause severe breathing difficulties which may not appear for several hours after exposure. Skin contact with selenium dioxide or selenium oxychloride may cause skin burns. Skin exposure to selenium dioxide dust may cause a skin rash. Splashes of selenium dioxide may cause eye irritation. Selenium dioxide dust may cause "rose eye," an allergy of the eyelids in which they may become puffy.

2. *Long-term Exposure:* Prolonged exposure to selenium, sodium selenite, sodium selenate, or selenium dioxide may cause paleness, coated tongue, stomach disorders, nervousness, metallic taste and a garlic odor of the breath. Fluid in the abdominal cavity, damage to the liver and spleen, and anemia have been reported in animals. Prolonged skin contact with selenium oxide or selenium oxychloride may cause skin sensitization.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Occupational Health Guideline for Selenium and Its Inorganic Compounds (as Selenium)*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to all selenium and its inorganic compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Selenium

- Formula: Se
- Synonyms: Selenium, metallic; selenium, elemental
- Appearance and odor: Black, gray, or red odorless solid.

Sodium selenite

- Formula: Na_2SeO_3
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Sodium selenate

- Formula: Na_2SeO_4
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Selenium dioxide

- Formula: SeO_2
- Synonyms: None
- Appearance and odor: Colorless and odorless solid.

Selenium oxychloride

- Formula: SeOCl_2
- Synonyms: None
- Appearance: Colorless to yellow liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

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HEALTH HAZARD INFORMATION

• Routes of exposure

Selenium, sodium selenite, sodium selenate, or selenium dioxide can affect the body if they are inhaled, if they come in contact with the eyes or skin, or if they are swallowed. Selenium oxychloride and selenium dioxide may enter the body through the skin.

• Effects of overexposure

1. *Short-term Exposure:* Inhalation of large quantities of selenium dioxide or selenium oxychloride may cause severe breathing difficulties which may not appear for several hours after exposure. Skin contact with selenium dioxide or selenium oxychloride may cause skin burns. Skin exposure to selenium dioxide dust may cause a skin rash. Splashes of selenium dioxide may cause eye irritation. Selenium dioxide dust may cause "rose eye," an allergy of the eyelids in which they may become puffy.

2. *Long-term Exposure:* Prolonged exposure to selenium, sodium selenite, sodium selenate, or selenium dioxide may cause paleness, coated tongue, stomach disorders, nervousness, metallic taste and a garlic odor of the breath. Fluid in the abdominal cavity, damage to the liver and spleen, and anemia have been reported in animals. Prolonged skin contact with selenium oxide or selenium oxychloride may cause skin sensitization.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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3. **Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to selenium and its inorganic compounds.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to selenium and its inorganic compounds at potentially hazardous levels:

1. **Initial Medical Examination:**

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to selenium, or with a history of other chronic respiratory disease, gastrointestinal disturbances, disorders of liver or kidneys, or recurrent dermatitis would be expected to be at increased risk from exposure. Examination of the eyes, respiratory system, liver, kidneys, and blood should be stressed. The skin should be examined for evidence of chronic disorders. Special consideration should be given to women of childbearing age since the possibility that selenium may be teratogenic might place these women in a high risk group.

—Urinalysis: Proper function of the kidneys is necessary to validate levels of selenium in the urine. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Selenium causes liver damage and tumors in animals. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. **Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

Elemental selenium and certain selenium compounds as dusts, vapors, and fumes irritate the eyes, upper respiratory tract, and skin. Animals exposed to selenium anhydride at a concentration of 150 mg/m³ for 4 hours developed conjunctivitis, pulmonary edema, and convulsions preceding death; there were degenerative changes in the liver, kidneys, spleen, and heart. Prolonged feeding of animals with diets containing selenium in amounts of 5 to 15 ppm caused hepatic necrosis, hemorrhage, and cirrhosis; marked and progressive anemia occurred in some species. The possibility of teratogenic effects from exposure to selenium has been raised, based upon observations in animals, but it has not been established in man. Eleven of 53 rats developed adenoma or low-grade carcinoma in cirrhotic livers, and four others had advanced adenomatoid hyperplasia, after having survived for 18 to 24 months on diets containing 5, 7, or 10 ppm of selenium; no tumors occurred in 73 rats surviving less than 18 months, although after 3 months cirrhosis was frequent. In

control rats 18 to 24 months of age, the incidence of spontaneous hepatic tumors was less than 1%. A group of workers briefly exposed to high concentrations of selenium fume developed severe irritation of the eyes, nose, and throat, followed by headaches; transient dyspnea occurred in one case. In workers exposed to an undetermined concentration of selenium oxide there was bronchospasm and dyspnea, followed within 12 hours by chills, fever, headache, and bronchitis, leading to pneumonitis in a few cases; all were asymptomatic within a week. In a study of workers in a selenium plant, workroom air levels ranged from 0.2 to 3.6 mg/m³, while urinary levels ranged from below 0.10 to 0.43 mg/l; the chief complaints were garlic odor of the breath, metallic taste, gastrointestinal disturbances, and skin eruptions. An accidental spray of selenium dioxide, in unspecified form and concentration, into the eyes of a chemist caused superficial burns of the skin and immediate irritation of the eyes; within 16 hours vision was blurred, and the lower portions of both corneas appeared dulled; 16 days after the accident the corneas were normal. Acute burns of the skin can be caused by selenium oxychloride and selenium oxide, which are highly vesicant. Contact with the fume of heated selenium dioxide caused an acute, weeping dermatitis, with the development of hypersensitivity in some cases.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Selenium**

1. Molecular weight: 78.96
2. Boiling point (760 mm Hg): 685 C (1265 F)
3. Specific gravity (water = 1): 4.45 to 4.8
4. Vapor density (air = 1 at boiling point of selenium): Not applicable
5. Melting point: 150 C (302 F)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium selenite**

1. Molecular weight: 173
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.1
4. Vapor density (air = 1 at boiling point of sodium selenite): Not applicable
5. Melting point: 710 C (1310 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 85
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium selenate**

1. Molecular weight: 188.9
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.1

3. **Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to selenium and its inorganic compounds.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to selenium and its inorganic compounds at potentially hazardous levels:

1. **Initial Medical Examination:**

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of asthma, allergies, or known sensitization to selenium, or with a history of other chronic respiratory disease, gastrointestinal disturbances, disorders of liver or kidneys, or recurrent dermatitis would be expected to be at increased risk from exposure. Examination of the eyes, respiratory system, liver, kidneys, and blood should be stressed. The skin should be examined for evidence of chronic disorders. Special consideration should be given to women of childbearing age since the possibility that selenium may be teratogenic might place these women in a high risk group.

—Urinalysis: Proper function of the kidneys is necessary to validate levels of selenium in the urine. A urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Selenium causes liver damage and tumors in animals. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

2. **Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

Elemental selenium and certain selenium compounds as dusts, vapors, and fumes irritate the eyes, upper respiratory tract, and skin. Animals exposed to selenium anhydride at a concentration of 150 mg/m³ for 4 hours developed conjunctivitis, pulmonary edema, and convulsions preceding death; there were degenerative changes in the liver, kidneys, spleen, and heart. Prolonged feeding of animals with diets containing selenium in amounts of 5 to 15 ppm caused hepatic necrosis, hemorrhage, and cirrhosis; marked and progressive anemia occurred in some species. The possibility of teratogenic effects from exposure to selenium has been raised, based upon observations in animals, but it has not been established in man. Eleven of 53 rats developed adenoma or low-grade carcinoma in cirrhotic livers, and four others had advanced adenomatoid hyperplasia, after having survived for 18 to 24 months on diets containing 5, 7, or 10 ppm of selenium; no tumors occurred in 73 rats surviving less than 18 months, although after 3 months cirrhosis was frequent. In

control rats 18 to 24 months of age, the incidence of spontaneous hepatic tumors was less than 1%. A group of workers briefly exposed to high concentrations of selenium fume developed severe irritation of the eyes, nose, and throat, followed by headaches; transient dyspnea occurred in one case. In workers exposed to an undetermined concentration of selenium oxide there was bronchospasm and dyspnea, followed within 12 hours by chills, fever, headache, and bronchitis, leading to pneumonitis in a few cases; all were asymptomatic within a week. In a study of workers in a selenium plant, workroom air levels ranged from 0.2 to 3.6 mg/m³, while urinary levels ranged from below 0.10 to 0.43 mg/l; the chief complaints were garlic odor of the breath, metallic taste, gastrointestinal disturbances, and skin eruptions. An accidental spray of selenium dioxide, in unspecified form and concentration, into the eyes of a chemist caused superficial burns of the skin and immediate irritation of the eyes; within 16 hours vision was blurred, and the lower portions of both corneas appeared dulled; 16 days after the accident the corneas were normal. Acute burns of the skin can be caused by selenium oxychloride and selenium oxide, which are highly vesicant. Contact with the fume of heated selenium dioxide caused an acute, weeping dermatitis, with the development of hypersensitivity in some cases.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data—Selenium**

1. Molecular weight: 78.96
2. Boiling point (760 mm Hg): 685 C (1265 F)
3. Specific gravity (water = 1): 4.45 to 4.8
4. Vapor density (air = 1 at boiling point of selenium): Not applicable
5. Melting point: 150 C (302 F)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium selenite**

1. Molecular weight: 173
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.1
4. Vapor density (air = 1 at boiling point of sodium selenite): Not applicable
5. Melting point: 710 C (1310 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 85
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Physical data—Sodium selenate**

1. Molecular weight: 188.9
2. Boiling point (760 mm Hg): Decomposes
3. Specific gravity (water = 1): 3.1

4. Vapor density (air = 1 at boiling point of sodium selenate): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
7. Solubility in water, g/200 g water at 20 C (68 F): 83
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Selenium dioxide**

1. Molecular weight: 110.9
2. Boiling point (760 mm Hg): 315 C (599 F) (sublimes)
3. Specific gravity (water = 1): 3.95
4. Vapor density (air = 1 at boiling point of selenium dioxide): Not applicable
5. Melting point: 340 C (644 F)
6. Vapor pressure at 20 C (68 F): 0.001 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 257
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Selenium oxychloride**

1. Molecular weight: 165.9
2. Boiling point (760 mm Hg): 176 C (349 F)
3. Specific gravity (water = 1): 2.42
4. Vapor density (air = 1 at boiling point of selenium oxychloride): 5.7
5. Melting point: 10.8 C (51 F)
6. Vapor pressure at 20 C (68 F): 0.35 mm approximately
7. Solubility in water, g/100 g water at 20 C (68 F): Decomposes
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: None hazardous
2. Incompatibilities: Contact of selenium with acids may cause formation of poisonous hydrogen selenide gas. Contact of selenium with strong oxidizing agents may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving selenium, sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride.
4. Special precautions: None

- **Flammability**

1. Flash point: Not applicable
2. Autoignition temperature: Selenium: Data not available; sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride: Not applicable
3. Flammable limits in air, % by volume: Not applicable
4. Extinguishant: For selenium, water

- **Warning properties**

The *Documentation of TLV's* notes that "Clinton reported intense irritation of eyes, nose, and throat, followed by headache, in a group of workers briefly exposed to

high concentrations of selenium fume." The ILO reports that "persons who work in atmospheres containing selenium dioxide dust may develop a condition known among the workers as 'rose eye,' a pink allergy of the eyelids, which often become puffy. There is usually also a conjunctivitis of the palpebral conjunctiva but rarely of the bulbar conjunctiva." The *Hygienic Information Guide* for selenium states that "in contact with the eye, selenium compounds exert a rapid irritant action leading to inflammation." Grant reports that both selenium dioxide and selenium sulfide can produce toxic effects on the eye. Quantitative information concerning air concentrations of selenium compounds which cause eye irritation is not available.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of selenium and its inorganic compounds on a filter, followed by treatment with acid and atomic absorption spectrophotometric analysis. An analytical method for selenium and its inorganic compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which

4. Vapor density (air = 1 at boiling point of sodium selenate): Not applicable
5. Melting point: Decomposes
6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
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 2. Incompatibilities: Contact of selenium with acids may cause formation of poisonous hydrogen selenide gas. Contact of selenium with strong oxidizing agents may cause fires and explosions.
 3. Hazardous decomposition products: Toxic gases and vapors may be released in a fire involving selenium, sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride.
 4. Special precautions: None
- **Flammability**
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 2. Autoignition temperature: Selenium: Data not available; sodium selenite, sodium selenate, selenium dioxide, and selenium oxychloride: Not applicable
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Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

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• In addition to respirator selection, a complete respiratory protection program should be instituted which

includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with selenium oxychloride or liquids containing selenium oxychloride.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with selenium, sodium selenite, sodium selenate, or liquids containing these compounds.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with selenium dioxide or liquids containing selenium dioxide, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with selenium oxychloride, sodium selenite, sodium selenate, or selenium dioxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where there is any possibility of exposure of an employee's body to selenium, selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Non-impervious clothing which becomes contaminated with selenium oxychloride should be removed immediately and not reworn until the selenium oxychloride is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of selenium dioxide, selenium oxychloride, or liquids containing these compounds contacting the eyes.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where sodium selenite, sodium selenate, or liquids containing these compounds may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to selenium oxychloride, selenium dioxide, or liquids containing these compounds, an eyewash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Workers subject to skin contact with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash any areas of the body which may have contacted selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds at the end of each work day.
- Skin that becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these substances should be promptly washed or showered to remove any contaminant.
- Skin that becomes contaminated with selenium oxychloride should be immediately washed or showered to remove any selenium oxychloride.
- Eating and smoking should not be permitted in areas where selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds are handled, processed, or stored.
- Employees who handle selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to selenium and its inorganic compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining recovery, and purification and manufacture of selenium compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment

includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with selenium oxychloride or liquids containing selenium oxychloride.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with selenium, sodium selenite, sodium selenate, or liquids containing these compounds.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with selenium dioxide or liquids containing selenium dioxide, where skin contact may occur.
- If employees' clothing has had any possibility of being contaminated with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with selenium oxychloride, sodium selenite, sodium selenate, or selenium dioxide should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of contaminant from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the contaminant, the person performing the operation should be informed of contaminant's hazardous properties.
- Where there is any possibility of exposure of an employee's body to selenium, selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide or liquids containing these compounds should be removed promptly and not reworn until the contaminant is removed from the clothing.
- Non-impervious clothing which becomes contaminated with selenium oxychloride should be removed immediately and not reworn until the selenium oxychloride is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of selenium dioxide, selenium oxychloride, or liquids containing these compounds contacting the eyes.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where sodium selenite, sodium selenate, or liquids containing these compounds may contact the eyes.

- Where there is any possibility that employees' eyes may be exposed to selenium oxychloride, selenium dioxide, or liquids containing these compounds, an eye wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Workers subject to skin contact with selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash any areas of the body which may have contacted selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds at the end of each work day.
- Skin that becomes contaminated with selenium, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these substances should be promptly washed or showered to remove any contaminant.
- Skin that becomes contaminated with selenium oxychloride should be immediately washed or showered to remove any selenium oxychloride.
- Eating and smoking should not be permitted in areas where selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds are handled, processed, or stored.
- Employees who handle selenium oxychloride, sodium selenite, sodium selenate, selenium dioxide, or liquids containing these compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to selenium and its inorganic compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining recovery, and purification and manufacture of selenium compounds	Local exhaust ventilation; general dilution ventilation; personal protective equipment

Operation	Controls	Operation	Controls
Use in glassware industry for decolorization of fiberglass, scientific glassware, vehicular tail lights, traffic and other signal lenses, and infrared equipment; use in manufacture of electrical components in welding, transformers, semiconductors, photoelectric cells, etc.	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use in manufacture of delayed action blasting caps	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of photography and photocopy devices; manufacture of dyes, pigments, and colored glazes for metal etching and for printing on glass	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use as solvents in paint and varnish removers; rubber, resin, and glue solvent; use for organic synthesis in oxidation, hydrogenation, and dehydrogenation	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of lubricating oils and extreme pressure lubricants as antioxidants and detergency improvers	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use in refining of copper, silver, gold, or nickel ores or during recycling of scrap metal	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber industry for manufacture and use as vulcanization accelerators and antioxidants; use in manufacture of pharmaceuticals, fungicides, and dermatitis control	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use in miscellaneous operations in manufacture of insect repellants, activators, hardeners, special ceramic materials, plasticizers, and mercury vapor detectors	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a catalyst for hardening fats for soaps, waxes, edible fats, and plastics	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use for preparation of feed additives for poultry and swine	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of insecticides, parasiticides, bactericides, and herbicides for agricultural and citrus crops	Local exhaust ventilation; general dilution ventilation; personal protective equipment		
Use in manufacture of flame-proofing agents on textiles and electric cables	Local exhaust ventilation; general dilution ventilation; personal protective equipment		

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If selenium or its inorganic compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

• Skin Exposure

If selenium or its inorganic compounds get on the skin, immediately wash the contaminated skin. If selenium, sodium selenite, sodium selenate, or selenium dioxide soak through the clothing, remove the clothing immediately and wash the skin. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of selenium sodium selenite, sodium selenate, or selenium dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.

Operation	Controls	Operation	Controls
Use in glassware industry for decolorization of fiberglass, scientific glassware, vehicular tail lights, traffic and other signal lenses, and infrared equipment; use in manufacture of electrical components in welding, transformers, semiconductors, photoelectric cells, etc.	Local exhaust ventilation; general dilution ventilation; personal protective equipment	Use in manufacture of delayed action blasting caps	Local exhaust ventilation; general dilution ventilation; personal protective equipment
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If selenium or its inorganic compounds get on the skin, immediately wash the contaminated skin. If selenium, sodium selenite, sodium selenate, or selenium dioxide soak through the clothing, remove the clothing immediately and wash the skin. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of selenium sodium selenite, sodium selenate, or selenium dioxide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.

Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When selenium, sodium selenite, sodium selenate, selenium oxychloride, or selenium dioxide have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If selenium or its inorganic compounds are spilled, the following steps should be taken:

1. Ventilate area of spill.

2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing selenium and its inorganic compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Selenium and its inorganic compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Selenium Compounds (as Se)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Selenium and Compounds," *Hygienic Guide Series*, Detroit, Michigan, 1959.

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* SPECIAL NOTE

Selenium and its inorganic compounds (as selenium) appear on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding their carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

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RESPIRATORY PROTECTION FOR SELENIUM AND ITS INORGANIC COMPOUNDS (AS SELENIUM)

Condition	Minimum Respiratory Protection* Required Above 0.2 mg/m ³
Particulate Concentration	
10 mg/m ³ or less	<p>A high efficiency particulate filter respirator with a full facepiece.</p> <p>Any supplied-air respirator with a full facepiece, helmet, or hood.</p> <p>Any self-contained breathing apparatus with a full facepiece.</p>
100 mg/m ³ or less	<p>A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.</p> <p>A powered air-purifying respirator with a high efficiency particulate filter and a full facepiece, helmet, or hood.</p>
Greater than 100 mg/m ³ or entry and escape from unknown concentrations	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p> <p>A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.</p>
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	<p>A high efficiency particulate filter respirator with a full facepiece.</p> <p>Any escape self-contained breathing apparatus with a full facepiece.</p>

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Silver Metal and Soluble Silver Compounds

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

APPLICABILITY

The general guidelines contained in this document apply to metallic silver and all soluble silver compounds. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

SUBSTANCE IDENTIFICATION

Silver, metallic

- Formula: Ag
- Synonyms: None
- Appearance and odor: Characteristic white metallic solid with no odor.

Silver nitrate

- Formula: AgNO_3
- Synonyms: Argerol; lunar caustic
- Appearance and odor: Colorless and odorless solid which may become gray on storage.

Silver fluoride

- Formula: AgF
- Synonyms: None
- Appearance and odor: Yellow-white, odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for silver metal and soluble silver compounds is 0.01 milligram of silver metal and soluble silver compounds per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. The American Conference of Governmental Industrial Hygienists has issued a Notice of Intended Changes of its recommended Threshold Limit Value for silver metal and soluble silver compounds from 0.01 mg/m^3 to 0.1 mg/m^3 .

HEALTH HAZARD INFORMATION

• Routes of exposure

Silver or soluble silver compounds can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

• Effects of overexposure

Silver or soluble silver compounds can cause discoloration or blue-gray darkening of the eyes, nose, throat, and skin. Silver nitrate is strongly corrosive and can cause burns and permanent damage to the eyes and can burn the skin.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to silver metal or soluble silver compounds.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to silver metal and soluble silver compounds at potentially hazardous levels:

1. Initial Medical Examination:

—Examination of the nasal septum, eyes, and skin for evidence of pigmentation: The purpose is to establish a baseline for future observations of silver deposition in tissues.

2. Periodic Medical Examination: The aforementioned

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

The dust of silver and its soluble compounds cause argyria, the local or generalized impregnation of the mucous membranes, skin, and eyes with silver. Localized argyria occurs in the skin, eyes, nasal septum and throat, where gray-blue patches of pigmentation are formed without evidence of tissue reaction. Generalized argyria is recognized by the widespread pigmentation of the skin and may be seen first in the conjunctiva, with some localization in the inner canthus. Argyrosis of the respiratory tract has been described in two workers involved in the manufacture of silver nitrate; their only symptom was mild, chronic bronchitis; bronchoscopy revealed tracheobronchial pigmentation; biopsy of the nasal mucous membrane showed silver deposition in the subepithelial area. A total body burden from 1 to 5 g of silver will lead to generalized argyria. Silver, once deposited in the body, is poorly excreted in the urine in amounts detectable by spectrochemical methods. Silver nitrate (lunar caustic) may cause irritation, ulcers, and discoloration of skin; if ingested, it may cause abdominal pain and gastroenteritis.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data—Silver, metallic**

1. Molecular weight: 107.9
2. Boiling point (760 mm Hg): 2200 C (3992 F)
3. Specific gravity (water = 1): 10.4
4. Vapor density (air = 1 at boiling point of metallic silver): Not applicable
5. Melting point: 966 C (1771 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Silver nitrate**

1. Molecular weight: 169.9
2. Boiling point (760 mm Hg): 444 C (831 F) (decomposes)
3. Specific gravity (water = 1): 4.4
4. Vapor density (air = 1 at boiling point of silver nitrate): Not applicable
5. Melting point: 209 C (408 F)
6. Vapor pressure at 20 C (68 F): Negligible
7. Solubility in water, g/100 g water at 20 C (68 F): 245
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Physical data—Silver fluoride**

1. Molecular weight: 126.9
2. Boiling point (760 mm Hg): 1159 C (2119 F) (approximately)
3. Specific gravity (water = 1): 5.8
4. Vapor density (air = 1 at boiling point of silver fluoride): Not applicable

5. Melting point: 435 C (815 F)

6. Vapor pressure at 20 C (68 F): Negligible

7. Solubility in water, g/100 g water at 20 C (68 F): 64

8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of metallic silver and soluble silver compounds with acetylene may cause formation of silver acetylide that is sensitive to shock. Contact with ammonia may cause formation of compounds that are explosive when dry. Contact with strong hydrogen peroxide solutions will cause violent decomposition to oxygen gas.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when some soluble silver compounds decompose.

4. Special precautions: Soluble silver compounds will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Most soluble silver compounds are not combustible. However, silver nitrate is a strong oxidizing material capable of increasing the flammability of combustible, organic, or other readily oxidizable materials. The following soluble silver compounds are explosives and should be stored and handled in accordance with 29 CFR 1910.109: silver acetylide, silver azide, silver fulminate, silver oxalate mixtures, silver styphnate, silver tartrate mixtures, and silver tetrazene.

- **Warning properties**

According to Stecher "many silver salts are irritating . . . to mucous membranes." Grant notes that many simple silver salts and silver ammonium compounds are injurious to the eye. According to Grant, "a great many reports have been published describing argyrosis of the eye, either from local contact with silver compounds or as a part of a generalized argyrosis from systemic absorption of silver or its compounds." Since there are inadequate data to assess the effects on the eye at or near the permissible exposure limit, for the purposes of this guideline, silver metal and soluble silver compounds are considered to have poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for silver metal and soluble silver

medical examinations should be repeated on an annual basis.

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- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for silver metal and soluble silver

compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with powdered metallic silver or solids or liquids containing soluble silver compounds, where skin contact may occur.
- If employees' clothing may have become contaminated with solids or liquids containing soluble silver compounds, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with metallic silver or soluble silver compounds should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of substances from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the substances, the person performing the operation should be informed of substances' hazardous properties.
- Non-impervious clothing which becomes contaminated with metallic silver or soluble silver compounds should be removed promptly and not reworn until the metallic silver or soluble silver compounds are removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of powdered metallic silver or solids or liquids containing soluble silver compounds contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to silver nitrate or solutions containing 5 percent or more silver nitrate by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with metallic silver or soluble silver compounds should be promptly

washed or showered to remove any metallic silver or soluble silver compounds.

- Eating and smoking should not be permitted in areas where metallic silver or solids or liquids containing soluble silver compounds are handled, processed, or stored.
- Employees who handle powdered metallic silver or solids or liquids containing soluble silver compounds should wash their hands thoroughly before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to silver metal and soluble silver compounds may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during mining and purification from ore; during refining from secondary sources	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in manufacture of silver nitrate for use in photography, mirrors, plating, inks, dyes, and porcelain; and as germicides, antiseptics, caustics, and analytical reagents	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of silver salts as catalysts in oxidation-reduction and polymerization reactions; in chemical synthesis; in glass manufacture, in silver-plating, in photography, as laboratory reagents, and in medicine	Process enclosure; local exhaust ventilation; personal protective equipment

compounds is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

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Use in manufacture of silver salts as catalysts in oxidation-reduction and polymerization reactions; in chemical synthesis; in glass manufacture, in silver-plating, in photography, as laboratory reagents, and in medicine	Process enclosure; local exhaust ventilation; personal protective equipment

Operation	Controls
Liberation from manufacture and casting of alloys; during fabrication of silver metal, alloys, and bi-metals for electrical uses; and during electroplating operations and fabrication of solders and brazing alloys; during manufacture and use of photographic chemicals and materials; during manufacture of mirrors, and during manufacture of silver powder pigments and paints	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use during manufacture of silver powder pigments and paints; during manufacture of mirrors; during manufacture of photographic chemicals and materials	Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If powdered metallic silver or solids or liquids containing soluble silver compounds get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If powdered metallic silver or solids or liquids containing soluble silver compounds get on the skin, flush the contaminated skin with water. If powdered metallic silver or solids or liquids containing soluble silver compounds penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention. Other silver compounds should be removed by promptly flushing the skin with water.

• Breathing

If a person breathes in large amounts of silver metal or soluble silver compounds, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

If silver nitrate or other corrosive soluble silver compounds have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the silver nitrate or other corrosive silver compounds. Do not attempt to make the exposed person vomit. Get medical attention immediately. When non-corrosive soluble silver compounds have been swallowed, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If powdered silver metal or soluble silver compounds are spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing silver metal or soluble silver compounds should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Silver metal and soluble silver compounds may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Silver," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- Browning, E.: *Toxicity of Industrial Metals* (2nd ed.), Butterworths, London, 1969.
- Buckley, W. R., et al.: "Localized Argyria. II. Clinical Nature of the Silver Containing Particles," *Archives of Dermatology*, 92:697-705, 1965.
- Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.
- Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.

Operation

Liberation from manufacture and casting of alloys; during fabrication of silver metal, alloys, and bi-metals for electrical uses; and during electroplating operations and fabrication of solders and brazing alloys; during manufacture and use of photographic chemicals and materials; during manufacture of mirrors, and during manufacture of silver powder pigments and paints

Use during manufacture of silver powder pigments and paints; during manufacture of mirrors; during manufacture of photographic chemicals and materials

Controls

Local exhaust ventilation; general dilution ventilation; personal protective equipment

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- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Stecher, P. G. (ed.): *The Merck Index* (8th ed.), Merck Co., Inc., Rahway, New Jersey, 1968.
- *Survey of Compounds Which Have Been Tested for Carcinogenic Activity*, U.S. Public Health Service Publication No. 149, Original, Supplements 1 and 2, 1961-1967, 1968-1969, and 1970-1971.

RESPIRATORY PROTECTION FOR SILVER METAL AND SOLUBLE SILVER COMPOUNDS

Condition	Minimum Respiratory Protection* Required Above 0.01 mg/m ³
Particulate Concentration	
0.5 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 mg/m ³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
20 mg/m ³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Particulate Concentration	
0.5 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
10 mg/m ³ or less	A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.
20 mg/m ³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 20 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
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Occupational Health Guideline for Zinc Oxide Fume

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: ZnO
- Synonyms: None
- Appearance: White fume.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for zinc oxide fume is 5 milligrams of zinc oxide fume per cubic meter of air (mg/m^3) averaged over an eight-hour work shift. NIOSH has recommended that the permissible exposure limit be changed to 5 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 15 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Zinc Oxide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Zinc oxide fume can affect the body if it is inhaled.

• Effects of overexposure

1. *Short-term Exposure:* Zinc oxide fume causes a flu-like illness called metal fume fever. Symptoms of metal fume fever include headache, fever, chills, muscle aches, nausea, vomiting, weakness, and tiredness. The symptoms usually start several hours after exposure. The attack may last 6 to 24 hours. Metal fume fever is more likely to occur after a period away from the job (after weekends or vacations). High levels of exposure to zinc oxide fume may cause a metallic or sweet taste in

the mouth, dryness and irritation of the throat, and coughing at the time of exposure.

2. *Long-term Exposure:* None known.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to zinc oxide fume.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to zinc oxide fume at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system should be stressed.

—14" x 17" chest roentgenogram: Zinc oxide fume may cause respiratory impairment. Persons with pulmonary disease may be more susceptible to the effect of zinc oxide fume. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Persons with pre-existing pulmonary disease may be more susceptible to the effects of zinc oxide fume. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing. Determination of zinc in the urine may be helpful in evaluating the extent of absorption.

• Summary of toxicology

Inhalation of zinc oxide fume causes an influenza-like illness termed metal fume fever. Heavy human exposure to zinc oxide fume may cause an immediate dryness and irritation of the throat, a sweet or metallic taste followed by substernal tightness and constriction in the chest, and a dry cough. Several hours following exposure the subject develops fever, lassitude, malaise, fatigue, frontal headache, low back pain, muscle cramps, and occasionally blurred vision, nausea, and vomiting.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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Physical examination reveals fever, eventually followed by perspiration and chills, dyspnea, rales throughout the chest, and tachycardia; in some instances there has been a reversible reduction in pulmonary vital capacity; there is usually leukocytosis, which may amount to 12,000 to 16,000/MM³. An attack usually subsides after 6 to 12 hours but may last for up to 24 hours; recovery is usually complete. Most workers rapidly develop an immunity to these attacks, but it is as quickly lost; attacks tend to be more severe on the first day of the work-week. Only freshly formed fume causes the illness, presumably because flocculation occurs in the air; the larger particles that form are deposited in the upper respiratory tract and do not penetrate deeply into the lungs. Chills have been reported in workers from exposure to concentrations of zinc oxide fume below 5 mg/m³.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 81.37
2. Boiling point (760 mm Hg): Solid sublimates
3. Specific gravity (water = 1): 5.6 (solid)
4. Vapor density (air = 1 at boiling point of zinc oxide fume): Not applicable
5. Melting point: Greater than 1800 C (greater than 3272 F)
6. Vapor pressure at 20 C (68 F): Not applicable
7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble (solid)
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: Zinc oxide fume may react violently with chlorinated rubber.
3. Hazardous decomposition products: None
4. Special precautions: None

• Flammability

1. Not combustible

• Warning properties

Zinc oxide fume is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

• Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected

airborne concentrations of zinc oxide fume. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of zinc oxide on a cellulose membrane filter, followed by solubilizing the zinc with nitric acid and analyzing by atomic absorption spectrophotometry. An analytical method for zinc oxide fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

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7. Solubility in water, g/100 g water at 20 C (68 F): Insoluble (solid)
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1. Conditions contributing to instability: None
2. Incompatibilities: Zinc oxide fume may react violently with chlorinated rubber.
3. Hazardous decomposition products: None
4. Special precautions: None

• Flammability

1. Not combustible

• Warning properties

Zinc oxide fume is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

• Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected

airborne concentrations of zinc oxide fume. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of zinc oxide on a cellulose membrane filter, followed by solublizing the zinc with nitric acid and analyzing by atomic absorption spectrophotometry. An analytical method for zinc oxide fume is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to zinc oxide fume may occur and control methods which may be effective in each case:

Operation

Liberation during brazing, welding, burning, and cutting of zinc and galvanized metals

Liberation from founding of brass, copper, and zinc, and galvanizing of iron and steel

Liberation from abrasive cleaning of galvanized metal surface

Liberating during use as a ceramic flux

Liberation during recovery of impure lead blast furnace slag; from manufacture of glass to increase brilliance and luster of glass

Liberation from use as an intermediate in manufacture of other zinc compounds; in manufacture of electronic devices

Liberation from use as a filler material in crushed stone industry

Controls

General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

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General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment

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LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of releases until cleanup has been completed.
- If potentially hazardous amounts of zinc oxide fume are inadvertently released, ventilate the area of the release to disperse the fume.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Zinc Oxide Fume," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
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- Turner, J. A.: "An Occupational Dermatoconiosis Among Zinc Oxide Workers," *Public Health Reports*, 36:2727-2732, 1921.
- Vallee, B. L.: "Zinc and Its Biological Significance," *A.M.A. Archives of Industrial Health*, 16:147-154, 1957.

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Breathing

If a person breathes in large amounts of zinc oxide fume, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

Operation

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RESPIRATORY PROTECTION FOR ZINC OXIDE FUME

Condition	Minimum Respiratory Protection* Required Above 5 mg/m ³
Particulate Concentration	
50 mg/m ³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
2,500 mg/m ³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 2,500 mg/m ³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Particulate Concentration	
50 mg/m ³ or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
250 mg/m ³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
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OCCUPATIONAL SAFETY AND HEALTH GUIDELINE FOR BENZENE POTENTIAL HUMAN CARCINOGEN

INTRODUCTION

This guideline summarizes pertinent information about benzene for workers, employers, and occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; therefore, readers are advised to regard these recommendations as general guidelines.

SUBSTANCE IDENTIFICATION

• **Formula:** C₆H₆

• **Structure:**



• **Synonyms:** Benzol, benzole, benzolene, bicarburet of hydrogen, carbon oil, coal naphtha

• **Identifiers:** CAS 71-43-2; RTECS CY1400000; DOT III4, label required: "Flammable Liquid"

• **Appearance and odor:** Colorless liquid with an aromatic odor

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 78.12
2. Boiling point (at 760 mmHg): 80.1°C (176°F)
3. Specific gravity (water = 1): 0.88
4. Vapor density (air = 1 at boiling point of benzene): 2.7
5. Melting point: 5.5°C (42°F)
6. Vapor pressure at 20°C (68°F): 75 mmHg
7. Solubility in water, g/100 g water at 20°C (68°F): 0.06
8. Evaporation rate (butyl acetate = 1): 5.1
9. Saturation concentration in air (approximate) at 25°C (77°F): 12.5% (125,000 ppm)
10. Ionization potential: 9.25 eV

• Reactivity

Incompatibilities: Benzene reacts with strong oxidizers including chlorine, oxygen, and bromine with iron.

2. Hazardous decomposition products: Toxic vapors and gases (e.g., carbon monoxide) may be released in a fire involving benzene.

3. Caution: Benzene will attack some forms of plastics, coatings, and rubber.

• Flammability

1. Flash point: -11.1°C (12°F) (closed cup)
2. Autoignition temperature: 498°C (928°F)
3. Flammable limits in air, % by volume: Lower, 1.4; upper, 7.1
4. Extinguishant: Alcohol foam, carbon dioxide, and dry chemical extinguishants are effective. Water may be an ineffective extinguishant but may be used to cool fire-exposed containers.
5. Class IB Flammable Liquid (29 CFR 1910.106), Flammability Rating 3 (NFPA)
6. Unusual fire and explosion hazards: Benzene liquid is flammable, and its vapors can easily form explosive mixtures. Flashbacks may occur along a vapor trail.

• Warning properties

1. Odor threshold: 12 ppm
2. Eye irritation levels: 3,000 ppm for 0.5-1 hour
3. Other information: 3,000 ppm may irritate nose and respiratory tract.
4. Evaluation of warning properties for respirator selection: Warning properties are not considered in recommending respirators for use with carcinogens.

EXPOSURE LIMITS

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for benzene is 1 part of benzene per million parts of air (PPM) as a time-weighted average (TWA) concentration over an 8-hour workshift; the short-term exposure limit is 5 ppm in any 15-minute sampling period. The National Institute for Occupational Safety and Health (NIOSH) recommends that benzene be controlled and handled as a potential human carcinogen in the workplace and that exposure be reduced to the lowest feasible limit. The NIOSH recommended exposure limit (REL) is 0.1 ppm [0.32 milligrams of benzene per cubic meter of air (mg/m³)] as an 8-hour TWA and 1 ppm (3.2 mg/m³) as a ceiling in any 15-minute sampling period. The NIOSH REL is the lowest con-

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Table 1.—Occupational exposure limits for benzene

	Exposure limits	
	ppm	mg/m ³
OSHA PEL TWA	1	—
Short-term exposure limit (15 min)	5	—
NIOSH REL (Ca)* TWA	0.1	0.32
Ceiling (15 min)	1	3.2
ACGIH TLV [®] TWA (A2)†	10	30

* (Ca): NIOSH recommends treating as a potential human carcinogen.

†(A2): Suspected human carcinogen.

HEALTH HAZARD INFORMATION

• Routes of exposure

Benzene may cause adverse health effects following exposure via inhalation, ingestion, or dermal or eye contact.

• Summary of toxicology

1. *Effects on animals:* Acute inhalation of benzene by rats, mice, or rabbits caused narcosis, spontaneous heart contractions (ventricular fibrillation), and death due to respiratory paralysis. Subchronic inhalation of benzene by rats produced decreased white blood cell counts, decreased bone marrow cell activity, increased red blood cell activity, and cataracts. In rats, chronic inhalation or oral administration of benzene produced cancers of the liver, mouth, and Zymbal gland. Inhalation of benzene by pregnant rats caused retardation of fetal development and increased fetal mortality.

2. *Effects on humans:* Acute inhalation exposure of benzene has caused nerve inflammation (polyneuritis), central nervous system depression, and cardiac sensitization. Chronic exposure to benzene has produced anorexia and irreversible injury to the blood-forming organs; effects include aplastic anemia and leukemia.

• Signs and symptoms of exposure

1. *Short-term (acute):* Exposure to benzene can cause dizziness, euphoria, giddiness, headache, nausea, staggering gait, weakness, drowsiness, respiratory irritation, pulmonary edema and pneumonia, gastrointestinal irritation, convulsions, and paralysis. Benzene can also cause irritation to the skin, eyes, and mucous membranes.

2. *Long-term (chronic):* Exposure to benzene can cause fatigue, nervousness, irritability, blurred vision, and labored breath-

ing. Repeated skin contact can cause redness, blistering, and dry, scaly dermatitis.

RECOMMENDED MEDICAL PRACTICES

• Medical surveillance program

Workers with potential exposures to chemical hazards should be monitored in a systematic program of medical surveillance intended to prevent or control occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety and health, earliest possible detection of adverse health effects, and referral of workers for diagnostic confirmation and treatment. The occurrence of disease (a "sentinel health event," SHE) or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures.

A medical surveillance program should include systematic collection and epidemiologic analysis of relevant environmental and biologic monitoring, medical screening, morbidity, and mortality data. This analysis may provide information about the relatedness of adverse health effects and occupational exposure that cannot be discerned from results in individual workers. Sensitivity, specificity, and predictive values of biologic monitoring and medical screening tests should be evaluated on an industry-wide basis prior to application in any given worker group. Intrinsic to a surveillance program is the dissemination of summary data to those who need to know, including employers, occupational health professionals, potentially exposed workers, and regulatory and public health agencies.

• Preplacement medical evaluation

Prior to placing a worker in a job with a potential for exposure to benzene, the physician should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, liver, and respiratory, nervous, and hematopoietic (blood-cell-forming) systems. The physician should obtain baseline values for the complete blood count and a stained differential count of all blood cell types. Medical surveillance for respiratory disease should be conducted by using the principles and methods recommended by NIOSH and the American Thoracic Society (ATS).

A preplacement medical evaluation is recommended in order to detect and assess preexisting or concurrent conditions which may be aggravated or result in increased risk when a worker is exposed to benzene at or below the NIOSH REL. The examining physician should consider the probable frequency, intensity, and duration of exposure, as well as the nature and degree of the condition, in placing such a worker. Such conditions, which should not be regarded as absolute contraindi-

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cations to job placement, include a history of chronic skin disease, concurrent dermatitis, or mild non-hemolytic anemia (e.g., mild iron-deficiency anemia).

- **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker report symptoms that may be attributed to exposure to benzene. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, liver, and respiratory, nervous, and hematopoietic (blood-cell-forming) systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

- **Medical practices recommended at the time of job transfer or termination.**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to benzene may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

- **Sentinel health events**

1. Acute SHE's include: Acute myeloid leukemia and contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Decrease in the number (neutropenia) or absence (agranulocytosis) of certain white blood cells in the peripheral circulation and/or in the bone marrow (aplastic anemia) and cancer of the red blood cells (erythro-leukemia).

MONITORING AND MEASUREMENT PROCEDURES

- **TWA exposure evaluation**

Measurements to determine worker exposure to benzene should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

- **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of benzene. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample. A minimum of three measurements

should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

- **Method**

Sampling and analysis may be performed by collecting benzene vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure benzene may also be used if available. A detailed sampling and analytical method for benzene may be found in the *NIOSH Manual of Analytical Methods* (method number 1500).

PERSONAL PROTECTIVE EQUIPMENT

Chemical protective clothing (CPC) should be selected after utilizing available performance data, consulting with the manufacturer, and then evaluating the clothing under actual use conditions.

Workers should be provided with and required to use CPC, gloves, and other appropriate protective clothing necessary to prevent skin contact with benzene.

SANITATION

Clothing which is contaminated with benzene should be removed immediately and placed in sealed containers for storage until it can be discarded or until provision is made for the removal of benzene from the clothing. If the clothing is to be laundered or cleaned, the person performing the operation should be informed of benzene's hazardous properties. Reusable clothing and equipment should be checked for residual contamination before reuse or storage.

A change room with showers, washing facilities, and lockers that permit separation of street and work clothes should be provided.

Workers should be required to shower following a workshift and prior to putting on street clothes. Clean work clothes should be provided daily.

Skin that becomes contaminated with benzene should be promptly washed with soap and water.

Workers who handle benzene should wash their faces, hands, and forearms thoroughly with soap and water before eating, smoking, or using toilet facilities.

The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to benzene may occur and control methods which may be effective in each case are listed in Table 2.

cations to job placement, include a history of chronic skin disease, concurrent dermatitis, or mild non-hemolytic anemia (e.g., mild iron-deficiency anemia).

• **Periodic medical screening and/or biologic monitoring**
Occupational health interviews and physical examinations should be performed at regular intervals. Additional examinations may be necessary should a worker report symptoms that may be attributed to exposure to benzene. The interviews, examinations, and appropriate medical screening and/or biologic monitoring tests should be directed at identifying an excessive decrease or adverse trend in the integrity and physiologic function of the skin, liver, and respiratory, nervous, and hematopoietic (blood-cell-forming) systems as compared to the baseline status of the individual worker or to expected values for a suitable reference population. The following tests should be used and interpreted according to standardized procedures and evaluation criteria recommended by NIOSH and the ATS: standardized questionnaires and tests of lung function.

• **Medical practices recommended at the time of job transfer or termination.**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic and laboratory tests which were conducted at the time of placement should be repeated at the time of job transfer or termination. Any changes in the worker's health status should be compared to those expected for a suitable reference population. Because occupational exposure to benzene may cause diseases of prolonged induction-latency, the need for medical surveillance may extend well beyond termination of employment.

• **Sentinel health events**

1. Acute SHE's include: Acute myeloid leukemia and contact and/or allergic dermatitis.
2. Delayed-onset SHE's include: Decrease in the number (neutropenia) or absence (agranulocytosis) of certain white blood cells in the peripheral circulation and/or in the bone marrow (aplastic anemia) and cancer of the red blood cells (erythro-leukemia).

MONITORING AND MEASUREMENT PROCEDURES

• **TWA exposure evaluation**

Measurements to determine worker exposure to benzene should be taken so that the TWA exposure is based on a single entire workshift sample or an appropriate number of consecutive samples collected during the entire workshift. Under certain conditions, it may be appropriate to collect several short-term interval samples (up to 30 minutes each) to determine the average exposure level. Air samples should be taken in the worker's breathing zone (air that most nearly represents that inhaled by the worker).

• **Ceiling concentration evaluation**

Measurements to determine worker exposure should be taken during periods of maximum expected airborne concentrations of benzene. Each measurement to determine the NIOSH REL (ceiling exposure) in the worker's breathing zone (air that most nearly represents that inhaled by the worker) should consist of a 15-minute sample. A minimum of three measurements

should be taken during one workshift, and the highest of all measurements taken is an estimate of the worker's exposure. If the periods of maximum exposure are not clearly defined, a statistical procedure which can be used as a peak exposure detection strategy is given in the *Occupational Exposure Sampling Strategy Manual*.

• **Method**

Sampling and analysis may be performed by collecting benzene vapors with charcoal tubes followed by desorption with carbon disulfide and analysis by gas chromatography. Direct-reading devices calibrated to measure benzene may also be used if available. A detailed sampling and analytical method for benzene may be found in the *NIOSH Manual of Analytical Methods* (method number 1500).

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The storage, preparation, dispensing, or consumption of food or beverages, the storage or application of cosmetics, the storage or use of smoking materials, or the storage or use of products for chewing should be prohibited in work areas.

COMMON OPERATIONS AND CONTROLS

Common operations in which exposure to benzene may occur and control methods which may be effective in each case are listed in Table 2.

Table 2.—Operations and methods of control for benzene

Operations	Controls
During the manufacture and processing of benzene; during use as a raw material in the production of aromatic compounds and derivatives	Process enclosure, local exhaust ventilation, personal protective equipment
During the use of chemicals in which benzene may be an impurity (e.g., naphthas, toluene, xylene)	Process enclosure, local exhaust ventilation, personal protective equipment
During the manufacture and use of motor fuel blends in which benzene is used as an ingredient; during use as an extracting solvent	Process enclosure (when possible), local exhaust ventilation, personal protective equipment, material substitution
During the preparation and use of paint and varnish removers, rubber cements, and lacquers	Process enclosure (when possible), local exhaust ventilation, personal protective equipment, material substitution

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate emergency procedures.

• Eye exposure

Where there is any possibility of a worker's eyes being exposed to benzene, an eye-wash fountain should be provided within the immediate work area for emergency use.

If benzene gets into the eyes, flush them immediately with large amounts of water for 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin exposure

Where there is any possibility of a worker's body being exposed to benzene, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

If benzene gets on the skin, wash it immediately with soap and water. If benzene penetrates the clothing, remove the clothing immediately and wash the skin with soap and water. Get medical attention promptly.

• Rescue

If a worker has been incapacitated, move the affected worker from the hazardous exposure. Put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILLS AND LEAKS

Workers not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

If benzene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities of liquids containing benzene, absorb on paper towels and place in an appropriate container.
4. Large quantities of liquids containing benzene may be absorbed in vermiculite, dry sand, earth, or a similar material and placed in an appropriate container.
5. Liquids containing benzene may be collected by vacuuming with an appropriate system. If a vacuum system is used, there should be no sources of ignition in the vicinity of the spill, and flashback prevention devices should be provided.

WASTE REMOVAL AND DISPOSAL

U.S. Environmental Protection Agency, Department of Transportation, and/or state and local regulations shall be followed to assure that removal, transport, and disposal are in accordance with existing regulations.

RESPIRATORY PROTECTION

It must be stressed that the use of respirators is the least preferred method of controlling worker exposure and should not normally be used as the only means of preventing or minimizing exposure during routine operations. However, there are some exceptions for which respirators may be used to control exposure: when engineering and work practice controls are not technically feasible, when engineering controls are in the process of being installed, or during emergencies and certain maintenance operations including those requiring confined-space entry (Table 3).

In addition to respirator selection, a complete respiratory protection program should be instituted which as a minimum complies with the requirements found in the OSHA Safety and Health Standards, 29 CFR 1910.134. A respiratory protection program should include as a minimum an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic environmental monitoring, maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program, including selection of the correct respirators, requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly.

Only respirators that have been approved by the Mine Safety and Health Administration (MSHA, formerly Mining Enforcement and Safety Administration) and by NIOSH should be used. **Remember! Air-purifying respirators will not protect from oxygen-deficient atmospheres.**

Table 2.—Operations and methods of control for benzene

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Table 3.—Respiratory protection for benzene

Condition	Minimum respiratory protection*
Any detectable concentration	<p>Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode</p> <p>Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode</p>
Planned or emergency entry into environments containing unknown or any detectable concentration	<p>Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode</p> <p>Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure-demand or other positive pressure mode</p>
Firefighting	Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive pressure mode
Escape only	<p>Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted organic canister</p> <p>Any appropriate escape-type self-contained breathing apparatus</p>

* Only NIOSH/MSHA-approved equipment should be used.

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Occupational Health Guideline for Bromoform

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CHBr_3
- Synonyms: Tribromomethane
- Appearance and odor: Colorless to yellow liquid with an odor like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for bromoform is 0.5 part of bromoform per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of bromoform per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

Bromoform can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

• Effects of overexposure

1. *Short-term Exposure:* Bromoform can cause irritation of the eyes, nose, and throat. Swallowing bromoform may also cause dizziness, disorientation and slurred speech, unconsciousness, and death.

2. *Long-term Exposure:* Bromoform may cause liver damage.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to bromoform.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to bromoform at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from bromoform exposure.

—Skin disease: Bromoform can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Bromoform has been reported to be a liver toxin in animals, and justifies consideration before exposing persons with impaired liver function.

—Kidney disease: Although bromoform is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of bromoform might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

Bromoform vapor is a respiratory irritant, a narcotic, and an hepatotoxin. A saturated atmosphere of 7000 ppm or more produced anesthesia in dogs in 8 minutes and death in 60 minutes, with evidence of respiratory irritation and liver damage. Human exposure to the vapor causes irritation of the eyes and throat. Accidental ingestion of the liquid by children produced central nervous system depression with coma and loss of reflexes; smaller doses led to listlessness, headache, and vertigo. Chronic effects have not been reported from

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to bromoform.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to bromoform at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from bromoform exposure.

—Skin disease: Bromoform can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Bromoform has been reported to be a liver toxin in animals, and justifies consideration before exposing persons with impaired liver function.

—Kidney disease: Although bromoform is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of bromoform might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

Bromoform vapor is a respiratory irritant, a narcotic, and an hepatotoxin. A saturated atmosphere of 7000 ppm or more produced anesthesia in dogs in 8 minutes and death in 60 minutes, with evidence of respiratory irritation and liver damage. Human exposure to the vapor causes irritation of the eyes and throat. Accidental ingestion of the liquid by children produced central nervous system depression with coma and loss of reflexes; smaller doses led to listlessness, headache, and vertigo. Chronic effects have not been reported from

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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industrial exposure. Skin absorption is said to have been demonstrated.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 252.8
2. Boiling point (760 mm Hg): 148 C (298 F)
3. Specific gravity (water = 1): 2.85
4. Vapor density (air = 1 at boiling point of bromoform): 8.7
5. Melting point: 7.8 C (46 F)
6. Vapor pressure at 20 C (68 F): 5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.1
8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Bromoform reacts with chemically active metals such as sodium, potassium, calcium, powdered aluminum, zinc, and magnesium, and strong caustics.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen bromide and bromine) may be released in a fire involving bromoform.
4. Special precautions: Liquid bromoform will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

According to Patty, bromoform has a chloroformlike odor and is highly irritating. Since the TLV for bromoform was determined by taking into consideration its irritant effects, for the purposes of this guideline, bromoform is treated as a material with adequate warning properties.

Bromoform is an eye irritant, according to the *Documentation of TLVs*.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of bromoform vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure bromoform may

be used. An analytical method for bromoform is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid bromoform.
- Non-impervious clothing which becomes contaminated with liquid bromoform should be removed promptly and not reworn until the bromoform is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid bromoform may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid bromoform should be promptly washed or showered with soap or mild detergent and water to remove any bromoform.
- Eating and smoking should not be permitted in areas where bromoform is handled, processed, or stored.
- Employees who handle bromoform should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

industrial exposure. Skin absorption is said to have been demonstrated.

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SANITATION

- Skin that becomes contaminated with liquid bromoform should be promptly washed or showered with soap or mild detergent and water to remove any bromoform.
- Eating and smoking should not be permitted in areas where bromoform is handled, processed, or stored.
- Employees who handle bromoform should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to bromoform may occur and control methods which may be effective in each case:

Operation	Controls
Use as a heavy liquid flotation agent in mineral separation-sedimentary petrographical surveys, geological assays, and purification of materials such as quartz	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in chemical and pharmaceutical synthesis in condensation reactions, and source of free radicals to initiate transformation of various compounds	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as an industrial solvent in liquid-solvent extractions in nuclear magnetic resonance studies	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a flame retardant in compositions for cellulose and in microencapsulation	General dilution ventilation
Use as a catalyst, initiator, or sensitizer in polymer production, irradiation reactions, and vulcanization of rubber	Local exhaust ventilation; general dilution ventilation
Use as an ingredient in pharmaceuticals or medicinal products	Material substitution

EMERGENCY FIRST AID PROCEDURES

In the event of an **emergency**, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If bromoform gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If bromoform gets on the skin, promptly wash the contaminated skin using soap or mild detergent and

water. If bromoform soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of bromoform, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When bromoform has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If bromoform is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Bromoform may be disposed of by absorbing it in vermiculite, dry sand, earth, or a similar material and disposing in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR BROMOFORM

Condition	Minimum Respiratory Protection* Required Above 0.5 ppm
Vapor Concentration	
25 ppm or less	<p>A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).</p> <p>A gas mask with a chin-style or a front- or back-mounted organic vapor canister.</p> <p>Any supplied-air respirator with a full facepiece, helmet, or hood.</p> <p>Any self-contained breathing apparatus with a full-facepiece.</p>
1000 ppm or less	<p>A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.</p>
Greater than 1000 ppm or entry and escape from unknown concentrations	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p> <p>A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.</p>
Fire Fighting	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p>
Escape	<p>Any gas mask providing protection against organic vapors.</p> <p>Any escape self-contained breathing apparatus.</p>

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Carbon Tetrachloride*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CCl_4
- Synonyms: Tetrachloromethane
- Appearance and odor: Colorless liquid with an ether-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for carbon tetrachloride is 10 parts of carbon tetrachloride per million parts of air (ppm) averaged over an eight-hour work shift, with an acceptable ceiling concentration of 25 ppm and a maximum allowable peak of 200 ppm for up to 5 minutes in any four-hour period. NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 2 ppm averaged over a one-hour period, and that carbon tetrachloride be regulated as an occupational carcinogen. The NIOSH Criteria Document for Carbon Tetrachloride should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Carbon tetrachloride can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

• Effects of overexposure

1. *Short-term Exposure:* Exposure to carbon tetrachloride may cause drowsiness, dizziness, incoordination, and unconsciousness. Delayed effects from short-term overexposure include damage to the heart, liver, and

kidneys. Symptoms of liver damage include yellow jaundice and dark urine. Eye contact with liquid carbon tetrachloride causes burning and intense irritation.

2. *Long-term Exposure:* Prolonged or repeated exposure may cause liver and kidney damage. Repeated or prolonged contact of the liquid with the skin may cause skin irritation.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to carbon tetrachloride.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to carbon tetrachloride at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of liver and kidneys should be stressed. The skin and eyes should be examined for evidence of chronic disorders.

—Liver function tests: Carbon tetrachloride causes liver damage. A profile of liver function should be obtained using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

• Summary of toxicology

Carbon tetrachloride vapor is a narcotic and causes severe damage to the liver and kidneys. In animals the primary damage from intoxication is to the liver, but in humans the majority of fatalities have been the result of renal injury with secondary cardiac failure. In humans, liver damage occurs more often after ingestion of the

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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liquid than after inhalation of the vapor. Human fatalities from acute renal damage have occurred after exposure for @1/2 to 1 hour to concentrations of 1000 to 2000 ppm. Cardiac arrhythmias have been reported. Exposure to high concentrations results in symptoms of central nervous system depression, including dizziness, vertigo, incoordination, and mental confusion; abdominal pain, nausea, vomiting, and diarrhea are frequent. Polycythemia followed by anemia and hemodilution may occur. Within a few days, jaundice may appear and liver injury progress to toxic necrosis. At the same time, acute nephritis occurs, and albumin, red and white blood cells, and casts appear in the urine; there may be oliguria, anuria, and increased nitrogen retention resulting in the development of uremia. There are several reports of adverse effects in workmen who were repeatedly exposed to concentrations between 25 and 30 ppm; nausea, vomiting, dizziness, drowsiness, and headache were frequently noted. The effects of carbon tetrachloride in humans who are addicted to alcohol are more severe than usual. No adverse symptoms resulted from repeated exposure to 10 ppm. The liquid splashed in the eye causes pain and minimal injury to the conjunctiva. Prolonged or repeated skin contact with the liquid may result in skin irritation. It can be absorbed through the intact skin of animals and humans in toxic amounts. Hepatomas have been reported in several animal species and in man.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 153.8
2. Boiling point (760 mm Hg): 76.8 C (170 F)
3. Specific gravity (water = 1): 1.59
4. Vapor density (air = 1 at boiling point of carbon tetrachloride): 5.3
5. Melting point: -23 C (-9 F)
6. Vapor pressure at 20 C (68 F): 91 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.08
8. Evaporation rate (butyl acetate = 1): 12.8

• Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: Carbon tetrachloride reacts with chemically active metals such as sodium, potassium, and magnesium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, phosgene, and carbon monoxide) may be released when carbon tetrachloride decomposes.

4. Special precautions: Liquid carbon tetrachloride will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Not combustible

• Warning properties

1. Odor Threshold: Carbon tetrachloride has an odor threshold of approximately 50 ppm, according to the *Hygienic Guide*.

2. Eye Irritation Level: Grant states that carbon tetrachloride is slightly irritating to the eyes, but does not mention the concentrations at which irritation occurs. In addition, carbon tetrachloride is "strongly suspected of causing retrobulbar neuritis, optic neuritis, and optic atrophy."

3. Evaluation of Warning Properties: Since the odor threshold of carbon tetrachloride is well above the permissible exposure, and since no quantitative data are available relating its warning properties to air concentrations, carbon tetrachloride is considered as a substance with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of carbon tetrachloride. Each measurement to determine short-duration ceiling levels should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure. Each measurement to determine a one-hour ceiling should consist of a one-hour sample or a series of consecutive samples totalling one hour.

• Peak Above Ceiling Evaluation

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of carbon tetrachloride. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure carbon tetrachloride may be used. An analytical method for carbon tetrachloride is in the

liquid than after inhalation of the vapor. Human fatalities from acute renal damage have occurred after exposure for @1/2 to 1 hour to concentrations of 1000 to 2000 ppm. Cardiac arrhythmias have been reported. Exposure to high concentrations results in symptoms of central nervous system depression, including dizziness, vertigo, incoordination, and mental confusion; abdominal pain, nausea, vomiting, and diarrhea are frequent. Polycythemia followed by anemia and hemodilution may occur. Within a few days, jaundice may appear and liver injury progress to toxic necrosis. At the same time, acute nephritis occurs, and albumin, red and white blood cells, and casts appear in the urine; there may be oliguria, anuria, and increased nitrogen retention resulting in the development of uremia. There are several reports of adverse effects in workmen who were repeatedly exposed to concentrations between 25 and 30 ppm; nausea, vomiting, dizziness, drowsiness, and headache were frequently noted. The effects of carbon tetrachloride in humans who are addicted to alcohol are more severe than usual. No adverse symptoms resulted from repeated exposure to 10 ppm. The liquid splashed in the eye causes pain and minimal injury to the conjunctiva. Prolonged or repeated skin contact with the liquid may result in skin irritation. It can be absorbed through the intact skin of animals and humans in toxic amounts. Hepatomas have been reported in several animal species and in man.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 153.8
2. Boiling point (760 mm Hg): 76.3 C (170 F)
3. Specific gravity (water = 1): 1.59
4. Vapor density (air = 1 at boiling point of carbon tetrachloride): 5.3
5. Melting point: -23 C (-9 F)
6. Vapor pressure at 20 C (68 F): 91 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.08
8. Evaporation rate (butyl acetate = 1): 12.8

• Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: Carbon tetrachloride reacts with chemically active metals such as sodium, potassium, and magnesium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, phosgene, and carbon monoxide) may be released when carbon tetrachloride decomposes.
4. Special precautions: Liquid carbon tetrachloride will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Not combustible

• Warning properties

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RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid carbon tetrachloride.
- Clothing wet with liquid carbon tetrachloride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of carbon tetrachloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the carbon tetrachloride, the person performing the operation should be informed of carbon tetrachloride's hazardous properties.
- Non-impervious clothing which becomes contaminated with liquid carbon tetrachloride should be removed promptly and not reworn until the carbon tetrachloride is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid carbon tetrachloride may contact the eyes.

SANITATION

- Skin that becomes wet with liquid carbon tetrachloride should be promptly washed or showered with soap or mild detergent and water to remove any carbon tetrachloride.
- Eating and smoking should not be permitted in areas where carbon tetrachloride is handled, processed, or stored.

- Employees who handle liquid carbon tetrachloride should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.
- Areas in which exposure to carbon tetrachloride can occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to carbon tetrachloride may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of fluorocarbons for aerosols, refrigerants, and fire extinguishants	Material substitution; process enclosure; local exhaust ventilation; personal protective equipment
Use as an agricultural grain fumigant and pesticide	Material substitution; personal protective equipment
Use in polymer technology as reaction medium, catalyst, chain transfer agent, and solvent for resins; in organic synthesis for chlorination of organic compounds in soap perfumery and insecticide industries	Process enclosure; local exhaust ventilation
Use as an industrial solvent for rubber cements, cable and semiconductor manufacture, separation of xylene isomers as components to reduce flammability	Material substitution; process enclosure; local exhaust ventilation; personal protective equipment
Use as a laboratory solvent	Material substitution; personal protective equipment
Use in metal recovery and catalyst regeneration	Process enclosure; local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If carbon tetrachloride gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present

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Use as an industrial solvent for rubber cements, cable and semiconductor manufacture, separation of xylene isomers as components to reduce flammability	Material substitution; process enclosure; local exhaust ventilation; personal protective equipment
Use as a laboratory solvent	Material substitution; personal protective equipment
Use in metal recovery and catalyst regeneration	Process enclosure; local exhaust ventilation

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after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If carbon tetrachloride gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If carbon tetrachloride soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of carbon tetrachloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When carbon tetrachloride has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If carbon tetrachloride is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.

2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- Waste disposal method:

Carbon tetrachloride may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

REFERENCES

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*** SPECIAL NOTE**

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RESPIRATORY PROTECTION FOR CARBON TETRACHLORIDE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
100 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
300 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 300 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Chlorobenzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_6H_5Cl
- Synonyms: Monochlorobenzene; chlorobenzol; phenyl chloride; MCB
- Appearance and odor: Colorless liquid with a mild aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chlorobenzene is 75 parts of chlorobenzene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 350 milligrams of chlorobenzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

Chlorobenzene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

• Effects of overexposure

1. *Short-term Exposure:* Chlorobenzene may cause drowsiness, incoordination, and unconsciousness. It may also cause irritation of the eyes, nose, and skin. Exposure to high levels might also cause liver damage.

2. *Long-term Exposure:* Prolonged or repeated skin contact with chlorobenzene liquid may cause skin burns. Prolonged or repeated exposure to this chemical might also result in liver, kidney, or lung damage.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms

and suspects that they are caused by exposure to chlorobenzene.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to chlorobenzene at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from chlorobenzene exposure.

—Skin disease: Chlorobenzene can cause dermatitis on exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Chlorobenzene is known as a liver toxin in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although chlorobenzene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of chlorobenzene might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

Chlorobenzene vapor is a narcotic. Cats exposed to 8,000 ppm showed severe narcosis after ½ hour and died 2 hours after removal from exposure, but 660 ppm for 1 hour was tolerated. Exposed animals showed eye and nose irritation, drowsiness, incoordination, and coma followed by death from the most severe exposures. Several species of animals exposed to 1,000 ppm for 7 hours/day, 5 days/week over a period of 44 days showed histopathologic changes in the lungs, liver, and

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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—Liver disease: Chlorobenzene is known as a liver toxin in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although chlorobenzene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of chlorobenzene might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

Chlorobenzene vapor is a narcotic. Cats exposed to 8,000 ppm showed severe narcosis after ½ hour and died 2 hours after removal from exposure, but 660 ppm for 1 hour was tolerated. Exposed animals showed eye and nose irritation, drowsiness, incoordination, and coma followed by death from the most severe exposures. Several species of animals exposed to 1,000 ppm for 7 hours/day, 5 days/week over a period of 44 days showed histopathologic changes in the lungs, liver, and

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kidneys, but at 475 ppm there was only slight liver histopathology in guinea pigs. Toxicologic studies and experience indicate that chlorobenzene does not cause the type of blood changes seen with benzene exposure. In man, eye and nasal irritation begin to occur at 200 ppm, and at that level the odor is pronounced and unpleasant; industrial experience indicates that occasional short exposures are not likely to result in more than minor skin irritation, but prolonged or frequently repeated contact may result in skin burns. In one case of accidental poisoning from ingestion of the liquid by a child there was pallor, cyanosis, and coma, followed by complete recovery. Occupational intoxication has not been reported.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 112.5
2. Boiling point (760 mm Hg): 132 C (270 F)
3. Specific gravity (water = 1): 1.1
4. Vapor density (air = 1 at boiling point of chlorobenzene): 3.9
5. Melting point: -44 C (-47 F)
6. Vapor pressure at 20 C (68 F): 8.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.05
8. Evaporation rate (butyl acetate = 1): 1

• Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving chlorobenzene.
4. Special precautions: Liquid chlorobenzene will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: 28.9 C (84 F) (closed cup)
2. Autoignition temperature: 638 C (1180 F)
3. Flammable limits in air, % by volume: Lower: 1.3; Upper: 7.1
4. Extinguishant: Carbon dioxide; dry chemical, foam

• Warning properties

According to both Deichmann and Gerarde and the *AIHA Hygienic Guide*, the odor of chlorobenzene is "barely perceptible" at 60 ppm, a concentration below that of the permissible exposure. Chlorobenzene is considered to have good warning properties. It is an eye irritant, as stated by Patty, but the exact concentrations at which this irritation occurs are not mentioned.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based

on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure chlorobenzene may be used. An analytical method for chlorobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid chlorobenzene.

• Clothing wet with liquid chlorobenzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chlorobenzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chlorobenzene, the person performing the operation should be informed of chlorobenzene's hazardous properties.

• Any clothing which becomes wet with liquid chlorobenzene should be removed immediately and not

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• Any clothing which becomes wet with liquid chlorobenzene should be removed immediately and not

reworn until the chlorobenzene is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid chlorobenzene may contact the eyes.

SANITATION

- Skin that becomes wet with liquid chlorobenzene should be promptly washed or showered with soap or mild detergent and water to remove any chlorobenzene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chlorobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of phenol in synthesis of polymeric materials	Local exhaust ventilation
Use as an intermediate in manufacture of ortho- and para-nitrobenzenes for use in dye manufacture; manufacture of DDT, aniline, picric acid, beta-chloroanthraquinone, and other chemicals; manufacture of rubber adhesives and adhesives	Process enclosure
Use as fiber swelling agent and dye carrier in textile processing	Local exhaust ventilation
Use as tar and grease remover in cleaning and degreasing operations	Local exhaust ventilation
Use as solvent in surface coatings and surface coating removers	Process enclosure; local exhaust ventilation; personal protective equipment
Use as extractant in manufacture of diisocyanates, rubber, perfumes, and pharmaceuticals	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If chlorobenzene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and

upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If chlorobenzene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chlorobenzene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of chlorobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

If chlorobenzene has been swallowed, do not induce vomiting. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If chlorobenzene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
 2. Ventilate area of spill or leak.
 3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Chlorobenzene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of chlorobenzene vapors are permitted.
- Waste disposal method:

Chlorobenzene may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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Use as fiber swelling agent and dye carrier in textile processing	Local exhaust ventilation
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Use as solvent in surface coatings and surface coating removers	Process enclosure; local exhaust ventilation; personal protective equipment
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RESPIRATORY PROTECTION FOR CHLOROBENZENE

Condition	Minimum Respiratory Protection* Required Above 75 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2400 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2400 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Chloroform*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CHCl_3
- Synonyms: Trichloromethane
- Appearance and odor: Colorless liquid with a pleasant, sweet odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chloroform is a ceiling level of 50 parts of chloroform per million parts of air (ppm). This may also be expressed as 240 milligrams of chloroform per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to a ceiling level of 2 ppm averaged over a one-hour period, and that chloroform be regulated as an occupational carcinogen. The NIOSH Criteria Document for Chloroform should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Chloroform can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

• Effects of overexposure

1. *Short-term Exposure:* Chloroform vapor may cause headache, drowsiness, vomiting, dizziness, unconsciousness, irregular heart beat, and death. Liver and kidney damage may also result from exposure to chloroform vapor. When splashed in the eye, chloroform causes pain and irritation. Swallowing chloroform is

followed immediately by severe burning of the mouth and throat, pain in the chest and abdomen, and vomiting. Depending on the amount swallowed, loss of consciousness and liver damage may follow.

2. *Long-term Exposure:* Prolonged exposure to chloroform may cause liver and kidney damage. Prolonged or repeated skin contact with the liquid may produce skin irritation.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chloroform.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to chloroform at potentially hazardous levels:

1. *Initial Medical Examination:*

— A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. A history of, or physical signs consistent with, chronic alcoholism probably constitutes such an increased risk. Examination of liver, kidneys, and heart should be stressed. The skin should be examined for evidence of chronic disorders.

— Liver function tests: A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

— Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

• Summary of toxicology

Chloroform vapor is a central nervous system depressant and is toxic to the liver and kidneys. It has been largely abandoned as an anesthetic agent because of the frequency of cardiac arrest during surgery and of

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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delayed death due to hepatic injury. An increased incidence of cardiac arrhythmias has been demonstrated during surgery in patients anesthetized with chloroform, as compared with other anesthetic agents; vapor concentrations were of the order of 22,500 ppm. Animals showed minor and reversible injury of liver and kidneys after repeated 7-hour exposures to concentrations of chloroform as low as 25 ppm, while 50 to 85 ppm produced more severe injury. Experimental human exposures showed that 14,000 to 16,000 ppm caused rapid loss of consciousness in man; 4100 ppm or less caused serious disorientation, while single exposures of 1000 ppm caused dizziness, nausea, and after-effects of fatigue and headache. Prolonged exposure to 80 to 240 ppm caused lassitude, digestive disturbances, and mental dullness, while 20 to 70 ppm produced milder symptoms. Of 68 chemical workers exposed regularly to concentrations of 2 to 205 ppm for 1 to 4 years, some 25% had hepatomegaly. This group of 68 exposed workers were found to be more susceptible to viral hepatitis than the general population. The hepatotoxicity of several chlorinated hydrocarbons has been shown to be potentiated by prior exposure to some aliphatic alcohols. This phenomenon has been demonstrated in mice exposed first to isopropyl alcohol by gavage and then to chloroform by intraperitoneal injection. A potentiating effect of ethyl alcohol ingestion on the toxicity of chloroform vapor in the occupational setting is suspected, but has not been proven in industrial practice. High concentrations of vapor cause conjunctival irritation and blepharospasm. Liquid chloroform splashed in the eye causes immediate burning pain and conjunctival irritation; the corneal epithelium may be injured, but regeneration is prompt, and the eye returns to normal in 1 to 3 days. The liquid has a defatting effect on the skin and may produce chronic irritation with drying and cracking. Liver tumors have been reported in animals.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 119.4
2. Boiling point (760 mm Hg): 61 C (142 F)
3. Specific gravity (water = 1): 1.49
4. Vapor density (air = 1 at boiling point of chloroform): 4.1
5. Melting point: -63.5 C (-82 F)
6. Vapor pressure at 20 C (68 F): 160 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.8
8. Evaporation rate (butyl acetate = 1): 11.6

- **Reactivity**

1. Conditions contributing to instability: In the presence of air and light, chloroform slowly reacts to form toxic phosgene and hydrogen chloride gases.
2. Incompatibilities: Chloroform reacts with strong caustics and chemically active metals such as aluminum, magnesium powder, sodium, or potassium.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, phosgene, and carbon monoxide) may be released when chloroform decomposes.

4. Special precautions: Liquid chloroform will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Not combustible

- **Warning properties**

1. Odor Threshold: Patty reports that the odor threshold of chloroform is approximately 200 to 300 ppm, and May reports an odor threshold of 200 ppm. The *Hygienic Guide*, however, gives an odor threshold of 50 ppm and states that "olfactory fatigue" occurs upon exposure.

2. Eye Irritation Level: Grant states that "in conscious individuals high concentrations of vapors of chloroform cause moderate sensation of stinging and irritation of the eyes, automatically inducing protective closure of the lids." The concentrations causing eye irritation are not mentioned. However, Patty does not give any indication that eye irritation occurs at concentrations even as high as 4096 ppm.

3. Evaluation of Warning Properties: Since there are no quantitative data relating the irritant effects of chloroform to air concentrations, and since olfactory fatigue occurs during exposure to chloroform, this material is treated as a substance with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **One-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average one-hour exposure is based on a single one-hour sample. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chloroform. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure chloroform may be used. An

delayed death due to hepatic injury. An increased incidence of cardiac arrhythmias has been demonstrated during surgery in patients anesthetized with chloroform, as compared with other anesthetic agents; vapor concentrations were of the order of 22,500 ppm. Animals showed minor and reversible injury of liver and kidneys after repeated 7-hour exposures to concentrations of chloroform as low as 25 ppm, while 50 to 85 ppm produced more severe injury. Experimental human exposures showed that 14,000 to 16,000 ppm caused rapid loss of consciousness in man; 4100 ppm or less caused serious disorientation, while single exposures of 1000 ppm caused dizziness, nausea, and after-effects of fatigue and headache. Prolonged exposure to 80 to 240 ppm caused lassitude, digestive disturbances, and mental dullness, while 20 to 70 ppm produced milder symptoms. Of 68 chemical workers exposed regularly to concentrations of 2 to 205 ppm for 1 to 4 years, some 25% had hepatomegaly. This group of 68 exposed workers were found to be more susceptible to viral hepatitis than the general population. The hepatotoxicity of several chlorinated hydrocarbons has been shown to be potentiated by prior exposure to some aliphatic alcohols. This phenomenon has been demonstrated in mice exposed first to isopropyl alcohol by gavage and then to chloroform by intraperitoneal injection. A potentiating effect of ethyl alcohol ingestion on the toxicity of chloroform vapor in the occupational setting is suspected, but has not been proven in industrial practice. High concentrations of vapor cause conjunctival irritation and blepharospasm. Liquid chloroform splashed in the eye causes immediate burning pain and conjunctival irritation; the corneal epithelium may be injured, but regeneration is prompt, and the eye returns to normal in 1 to 3 days. The liquid has a defatting effect on the skin and may produce chronic irritation with drying and cracking. Liver tumors have been reported in animals.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 119.4
2. Boiling point (760 mm Hg): 61 C (142 F)
3. Specific gravity (water = 1): 1.49
4. Vapor density (air = 1 at boiling point of chloroform): 4.1
5. Melting point: -63.5 C (-82 F)
6. Vapor pressure at 20 C (68 F): 160 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.8
8. Evaporation rate (butyl acetate = 1): 11.6

• Reactivity

1. Conditions contributing to instability: In the presence of air and light, chloroform slowly reacts to form toxic phosgene and hydrogen chloride gases.
2. Incompatibilities: Chloroform reacts with strong caustics and chemically active metals such as aluminum, magnesium powder, sodium, or potassium.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, phosgene, and carbon monoxide) may be released when chloroform decomposes.

4. Special precautions: Liquid chloroform will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Not combustible

• Warning properties

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analytical method for chloroform is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent skin contact with liquid chloroform, where skin contact may occur.
- Clothing wet with liquid chloroform should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of chloroform from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chloroform, the person performing the operation should be informed of chloroform's hazardous properties.
- Non-impervious clothing which becomes wet with liquid chloroform should be removed promptly and not reworn until the chloroform is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid chloroform may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to chloroform, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid chloroform should be promptly washed or showered with soap or mild detergent and water to remove any chloroform.

- Eating and smoking should not be permitted in areas where liquid chloroform is handled, processed, or stored.
- Employees who handle liquid chloroform should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.
- Areas in which exposure to chloroform may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized persons.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chloroform may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of fluorocarbons for refrigerant propellants; manufacture of fluorocarbon resins	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as an extractant solvent in manufacture of pharmaceuticals, rubber, essential oils and flavors, sterols and alkaloids, and in the recovery of fat from waste products	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in chemical analysis and assays; veterinary uses, and in standard solutions as preservative and bactericide	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a general solvent in plastics, dyes, oils, waxes, rubber, cleaning and dry cleaning industries	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in dye, drug, and pesticide industries	Process enclosure; local exhaust ventilation; general dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If chloroform gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If burning is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

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Use as a general solvent in plastics, dyes, oils, waxes, rubber, cleaning and dry cleaning industries	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a chemical intermediate in dye, drug, and pesticide industries	Process enclosure; local exhaust ventilation; general dilution ventilation

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- **Skin Exposure**

If chloroform gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If chloroform soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of chloroform, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When chloroform has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If chloroform is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

ADDITIONAL INFORMATION

To find additional information on chloroform, look up chloroform in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for Chloroform (Revised June 1976)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Chloroform," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Chloroform," *Hygienic Guide Series*, Detroit, Michigan, 1965.
- Dow Chemical Company: *Material Safety Data Sheet - Chloroform*, Midland, Michigan.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- International Agency for Research on Cancer: *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Vol. 1, Lyon, France, 1972.
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- Lehman, K. B., and Schmidt-Kerl, L.: "The Thirteen Most Important Chlorinated Aliphatic Hydrocarbons from the Standpoint of Industrial Hygiene," *Archives of Hygiene*, 116:131-200, 1936 (Ger.)
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- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard . . . Occupational Exposure to Chloroform*, HEW Publication No. (NIOSH) 75-114, GPO No. 017-033-00045, U.S. Government Printing Office, Washington, D.C., 1976 (revised).
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
- Traiger, G. J., and Plaa, G. L.: "Chlorinated Hydrocarbon Toxicity," *Archives of Environmental Health*, 28:276-278, 1974.
- von Oettingen, W. F.: *Poisoning: A Guide to Clinical Diagnosis and Treatment* (2nd ed.), Saunders, Philadelphia, 1958.

* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 1, 1972.

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RESPIRATORY PROTECTION FOR CHLOROFORM

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
500 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for o-Dichlorobenzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: 1,2- $C_6H_4Cl_2$
- Synonyms: 1,2-Dichlorobenzene; o-dichlorobenzol
- Appearance and odor: Colorless to pale yellow liquid with a pleasant aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for o-dichlorobenzene is a ceiling of 50 parts of o-dichlorobenzene per million parts of air (ppm). This may also be expressed as 300 milligrams of o-dichlorobenzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

o-Dichlorobenzene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may also be absorbed through the skin.

• Effects of overexposure

1. *Short-term Exposure:* o-Dichlorobenzene vapor may cause irritation of the upper respiratory tract and eyes. Higher concentrations may cause drowsiness, unconsciousness, and death. The liquid may cause burning of the skin. The liquid may also cause burning of the eyes with tissue damage.

2. *Long-term Exposure:* Prolonged or repeated contact with o-dichlorobenzene may cause skin irritation. Prolonged or repeated inhalation of high concentrations of vapor might cause liver or kidney injury.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to o-dichlorobenzene.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to o-dichlorobenzene at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from o-dichlorobenzene exposure.

—Liver disease: o-Dichlorobenzene is known as a liver toxin in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: o-Dichlorobenzene is known as a kidney toxin in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Skin disease: o-Dichlorobenzene may cause sensitization dermatitis and blistering of the skin. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

o-Dichlorobenzene vapor at high concentrations is toxic to the liver and kidneys in animals. Rats died from exposure to 977 ppm for 7 hours, but survived when exposed for only 2 hours; animals survived exposure to 539 ppm for 3 hours and at necropsy showed marked centrilobular necrosis of the liver, as well as cloudy swelling of the tubular epithelium of the kidneys. Several species of animals exposed repeatedly to 93 ppm for 7 hours daily showed no adverse effects. The liquid instilled in the rabbit eye produced apparent distress and slight conjunctival irritation. Eye irritation is not

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
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usually evident below 20 ppm but becomes noticeable at 25 to 30 ppm and painful to some at 60 to 100 ppm if exposures are for more than a few minutes duration. Some acclimatization may occur, but its extent is not great. Workers exposed daily to an average of 15 ppm showed no indication of injury. The liquid left on the skin may produce blistering. Sensitization dermatitis has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 147
2. Boiling point (760 mm Hg): 180 C (356 F)
3. Specific gravity (water = 1): 1.3
4. Vapor density (air = 1 at boiling point of o-dichlorobenzene): 5.1
5. Melting point: -17.6 C (0.5 F)
6. Vapor pressure at 20 C (68 F): 1.2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.015
8. Evaporation rate (butyl acetate = 1): Less than 1

• Reactivity

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Contact with strong oxidizers or with hot aluminum or aluminum alloys may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, chlorine, and carbon monoxide) may be released in a fire involving o-dichlorobenzene.
4. Special precautions: Liquid o-dichlorobenzene will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: 66 C (151 F) (closed cup)
2. Autoignition temperature: 648 C (1198 F)
3. Flammable limits in air, % by volume: Lower: 2.2; Upper: 9.2
4. Extinguishant: Dry chemical, foam, carbon dioxide

• Warning properties

1. Odor Threshold: 2 to 4 ppm, according to the AIHA *Hygienic Guide*; 50 ppm, according to May and Patty.
2. Eye Irritation Level: 20 to 30 ppm according to the AIHA *Hygienic Guide*.
3. Evaluation of Warning Properties: Since the odor threshold of o-dichlorobenzene and the concentration causing eye irritation are at or below the permissible exposure, it is treated as a material with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of o-dichlorobenzene. Each

measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure o-dichlorobenzene may be used. An analytical method for o-dichlorobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6). ical Methods for Set J" (order number PB 263 959).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid o-dichlorobenzene.
- Clothing wet with liquid o-dichlorobenzene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of o-dichlorobenzene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the o-dichlorobenzene, the person performing the operation should be informed of o-dichlorobenzene's hazardous properties.

usually evident below 20 ppm but becomes noticeable at 25 to 30 ppm and painful to some at 60 to 100 ppm if exposures are for more than a few minutes duration. Some acclimatization may occur, but its extent is not great. Workers exposed daily to an average of 15 ppm showed no indication of injury. The liquid left on the skin may produce blistering. Sensitization dermatitis has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 147
2. Boiling point (760 mm Hg): 180 C (356 F)
3. Specific gravity (water = 1): 1.3
4. Vapor density (air = 1 at boiling point of o-dichlorobenzene): 5.1
5. Melting point: -17.6 C (0.5 F)
6. Vapor pressure at 20 C (68 F): 1.2 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.015
8. Evaporation rate (butyl acetate = 1): Less than 1

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- Non-impervious clothing which becomes contaminated with liquid o-dichlorobenzene should be removed promptly and not reworn until the o-dichlorobenzene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid o-dichlorobenzene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid o-dichlorobenzene should be promptly washed or showered with soap or mild detergent and water to remove any o-dichlorobenzene.
- Employees who handle liquid o-dichlorobenzene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to o-dichlorobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Use in cleaning and degreasing of metal, leather, wool, paper, dry cleaning, brick, and upholstery	General dilution ventilation; personal protective equipment
Use as fumigant for poultry houses and stockyards for termites, moths, and beetles	Personal protective equipment
Use in application or removal of surface coatings	General dilution ventilation; personal protective equipment
Use in maintenance of equipment containing heat-transfer agents	Personal protective equipment
Use in organic synthesis in pesticides, herbicides, dyestuffs, and pharmaceuticals; chemical intermediate in manufacture of toluene-diisocyanate and extractive distillation of ethyl benzene from xylene; use as a deodorizing agent	General dilution ventilation

Operation

Use in textile dyeing operations

Controls

Local exhaust ventilation; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If liquid o-dichlorobenzene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If liquid o-dichlorobenzene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If liquid o-dichlorobenzene soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of o-dichlorobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When o-dichlorobenzene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If o-dichlorobenzene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.

- Non-impervious clothing which becomes contaminated with liquid o-dichlorobenzene should be removed promptly and not reworn until the o-dichlorobenzene is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where liquid o-dichlorobenzene may contact the eyes.

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Use as fumigant for poultry houses and stockyards for termites, moths, and beetles	Personal protective equipment
Use in application or removal of surface coatings	General dilution ventilation; personal protective equipment
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- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If o-dichlorobenzene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.

2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

- Waste disposal methods:

o-Dichlorobenzene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.
2. By atomizing in a suitable combustion chamber equipped with an effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "o-Dichlorobenzene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR o-DICHLOROBENZENE

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
1700 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 1700 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for p-Dichlorobenzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: 1,4- $C_6H_4Cl_2$
- Synonyms: 1,4-Dichlorobenzene; dichloride; PDCB
- Appearance and odor: Colorless solid with a moth-ball-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for p-dichlorobenzene is 75 parts of p-dichlorobenzene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 450 milligrams of p-dichlorobenzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

p-Dichlorobenzene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

• Effects of overexposure

Exposure to p-dichlorobenzene may cause irritation of the eyes, nose, and throat. It may also cause headache, swelling around the eyes, and runny nose. In addition, it may cause loss of appetite, nausea, vomiting, weight loss, and liver damage with yellow jaundice and death. Particles of solid p-dichlorobenzene in contact with the eyes may cause pain. The solid material also produces a burning sensation when held in contact with the skin with slight irritation. Warm fumes or strong solutions of p-dichlorobenzene may irritate the skin slightly on

prolonged or repeated contact. Red blotching of the skin due to allergy to p-dichlorobenzene may occur.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to p-dichlorobenzene.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to p-dichlorobenzene at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver, respiratory tract, eyes, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Since liver damage has been observed in humans exposed to p-dichlorobenzene, a profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Measurement of 2,5-dichlorophenol may serve as an index of exposure.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• Summary of toxicology

p-Dichlorobenzene vapor irritates the eyes and upper respiratory tract and is toxic to the liver. A group of animals repeatedly exposed to 798 ppm developed eye irritation, marked tremors, weakness, and loss of weight; some died. Reversible, nonspecific changes in the eye grounds were noted in rabbits, but there were no lens changes; other effects were centrolobular necrosis of the liver and mild damage to the lungs and kidneys. In five cases of intoxication from exposure to p-dichlorobenzene used as a mothproofing agent, one person with only moderate exposure complained of severe headache, periorbital swelling, and profuse rhinitis, which subsided 24 hours after cessation of exposure.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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The other four persons who had more prolonged exposure developed anorexia, nausea, vomiting, weight loss, and hepatic necrosis with jaundice; two died, and another developed cirrhosis. In 58 workers exposed for an average of 4.8 years (range, 8 months to 25 years) to p-dichlorobenzene at levels of 10 to 725 ppm, there was no evidence of hematologic effects; painful irritation of the eyes and nose was recorded at levels between 50 and 80 ppm, and it was severe at 160 ppm. Solid particles of p-dichlorobenzene in the human eye cause pain. The solid material produces a burning sensation when held in contact with the skin, but the resulting irritation is slight; warm fumes or strong solutions may irritate the intact skin slightly on prolonged or repeated contact. A case of allergic purpura induced by p-dichlorobenzene has been reported. In a study of workers engaged in synthesizing or otherwise handling p-dichlorobenzene, it was concluded that urinary excretion of 2,5-dichlorophenol (a metabolite of paradichlorobenzene) can serve as an index of exposure. Published studies of tests for carcinogenicity are considered to have been too short in duration and involved too few animals to have any significance.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 147
2. Boiling point (760 mm Hg): 174 C (345 F)
3. Specific gravity (water = 1): 1.46
4. Vapor density (air = 1 at boiling point of p-dichlorobenzene): 5.1
5. Melting point: 53 C (127 F)
6. Vapor pressure at 20 C (68 F): 0.4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.008
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving p-dichlorobenzene.
4. Special precautions: Liquid p-dichlorobenzene will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: 65.6 C (150 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 2.5 (calculated at flash point)
4. Extinguishant: Foam, carbon dioxide, dry chemical

• Warning properties

1. Odor Threshold: Patty states that "p-dichlorobenzene has a very distinctive aromatic odor. The threshold of detection will vary from 15 to 30 ppm in air. The odor becomes very strong at concentrations between 30

and 60 ppm It should be recognized, however, that a person may become sufficiently accustomed to the odor to tolerate high concentrations."

2. Irritation Levels: Patty states that p-dichlorobenzene "is painful to the eyes and nose at concentrations of 80 to 160 ppm. Above 160 ppm, it is intolerable to any person who has not worked in it long enough to have had some adaptation."

3. Evaluation of Warning Properties: Through its odor and irritant effects, p-dichlorobenzene can be detected within three times the permissible exposure limit. For the purposes of this guideline, therefore, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure p-dichlorobenzene may be used. An analytical method for p-dichlorobenzene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which

The other four persons who had more prolonged exposure developed anorexia, nausea, vomiting, weight loss, and hepatic necrosis with jaundice; two died, and another developed cirrhosis. In 58 workers exposed for an average of 4.8 years (range, 8 months to 25 years) to p-dichlorobenzene at levels of 10 to 725 ppm, there was no evidence of hematologic effects; painful irritation of the eyes and nose was recorded at levels between 50 and 80 ppm, and it was severe at 160 ppm. Solid particles of p-dichlorobenzene in the human eye cause pain. The solid material produces a burning sensation when held in contact with the skin, but the resulting irritation is slight; warm fumes or strong solutions may irritate the intact skin slightly on prolonged or repeated contact. A case of allergic purpura induced by p-dichlorobenzene has been reported. In a study of workers engaged in synthesizing or otherwise handling p-dichlorobenzene, it was concluded that urinary excretion of 2,5-dichlorophenol (a metabolite of paradichlorobenzene) can serve as an index of exposure. Published studies of tests for carcinogenicity are considered to have been too short in duration and involved too few animals to have any significance.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 147
2. Boiling point (760 mm Hg): 174 C (345 F)
3. Specific gravity (water = 1): 1.46
4. Vapor density (air = 1 at boiling point of p-dichlorobenzene): 5.1
5. Melting point: 53 C (127 F)
6. Vapor pressure at 20 C (68 F): 0.4 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.008
8. Evaporation rate (butyl acetate = 1): Not applicable

• Reactivity

1. Conditions contributing to instability: None
2. Incompatibilities: None
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving p-dichlorobenzene.
4. Special precautions: Liquid p-dichlorobenzene will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: 65.6 C (150 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 2.5 (calculated at flash point)
4. Extinguishant: Foam, carbon dioxide, dry chemical

• Warning properties

1. Odor Threshold: Patty states that "p-dichlorobenzene has a very distinctive aromatic odor. The threshold of detection will vary from 15 to 30 ppm in air. The odor becomes very strong at concentrations between 30

and 60 ppm It should be recognized, however, that a person may become sufficiently accustomed to the odor to tolerate high concentrations."

2. Irritation Levels: Patty states that p-dichlorobenzene "is painful to the eyes and nose at concentrations of 80 to 160 ppm. Above 160 ppm, it is intolerable to any person who has not worked in it long enough to have had some adaptation."

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- In addition to respirator selection, a complete respiratory protection program should be instituted which

includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solid particles or vapors from the surface of hot p-dichlorobenzene.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where p-dichlorobenzene or liquids containing p-dichlorobenzene may contact the eyes.

SANITATION

- Workers subject to skin contact with p-dichlorobenzene should wash any areas of the body which may have contacted p-dichlorobenzene at the end of each work day.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to p-dichlorobenzene may occur and control methods which may be effective in each case:

Operation	Controls
Formulation for use in moth control; as a deodorant for garbage and rest rooms; as an insecticide for control of fruit borers and ants; use in organic synthesis for preparation of dye intermediates	General dilution ventilation; local exhaust ventilation; personal protective equipment
Manufacture of p-dichlorobenzene	General dilution ventilation; local exhaust ventilation; personal protective equipment
Application as an insecticide, air deodorant, moth and mildew preventive, and household fumigant	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If p-dichlorobenzene or liquids containing p-dichlorobenzene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get

medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If p-dichlorobenzene or liquids containing p-dichlorobenzene get on the skin, wash the contaminated skin using soap or mild detergent and water. If p-dichlorobenzene or liquids containing p-dichlorobenzene penetrate through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of p-dichlorobenzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When p-dichlorobenzene has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

- If p-dichlorobenzene is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dispose in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device as in below or deposit in a secured sanitary landfill.

- Waste disposal methods:

p-Dichlorobenzene may be disposed of:

1. By making packages of p-dichlorobenzene in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving p-dichlorobenzene in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

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3. By disposal in a secured sanitary landfill.

REFERENCES

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RESPIRATORY PROTECTION FOR p-DICHLOROBENZENE

Condition	Minimum Respiratory Protection* Required Above 75 ppm
Vapor Concentration	
1,000 ppm or less	<p>A chemical cartridge respirator with a full facepiece, an organic vapor cartridge(s), and dust filter.</p> <p>A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust filter.</p> <p>Any supplied-air respirator with a full facepiece, helmet, or hood.</p> <p>Any self-contained breathing apparatus with a full facepiece.</p>
Greater than 1,000 ppm or entry and escape from unknown concentrations	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p> <p>A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.</p>
Fire Fighting	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p>
Escape	<p>Any gas mask providing protection against organic vapors and particulates.</p> <p>Any escape self-contained breathing apparatus.</p>

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for 1,1-Dichloroethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_3CHCl_2
- Synonyms: Asymmetrical dichloroethane; ethylidene chloride; 1,1-ethylidene dichloride
- Appearance and odor: Colorless liquid with a chloroform-like odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1-dichloroethane is 100 parts of 1,1-dichloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 400 milligrams of 1,1-dichloroethane per cubic meter of air (mg/m^3). The American Conference of Governmental Industrial Hygienists has recommended for 1,1-dichloroethane a Threshold Limit Value of 200 ppm.

HEALTH HAZARD INFORMATION

• Routes of exposure

1,1-Dichloroethane can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

• Effects of overexposure

1. *Short-term Exposure:* Breathing 1,1-dichloroethane vapor may cause drowsiness and unconsciousness. It might also cause damage to the liver, kidneys, and lungs. Splashing the liquid in the eyes may cause irritation.

2. *Long-term Exposure:* Prolonged, confined, or repeated skin contact with 1,1-dichloroethane can produce a slight burn.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1-dichloroethane.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to 1,1-dichloroethane at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,1-dichloroethane exposure.

—Skin disease: 1,1-Dichloroethane can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although 1,1-dichloroethane is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although 1,1-dichloroethane is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,1-dichloroethane might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

1,1-Dichloroethane vapor is a narcotic. Rats exposed to 32,000 ppm for 30 minutes did not survive. The most consistent findings in animals exposed to concentrations

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

of above 8,000 ppm for up to 7 hours were pathologic changes in the kidney and liver, and at much higher concentrations, near 64,000 ppm, damage to the lungs as well. Repeated daily exposure of several species of animals to 1,000 ppm resulted in no pathologic or hematologic changes. The liquid applied to the intact or abraded skin of rabbits produced slight edema and very slight necrosis after six daily applications. Instilled in the eyes of rabbits there was immediate, moderate conjunctival irritation and swelling which subsided within a week. There have been no reported cases of human overexposure by inhalation; prolonged, confined, or repeated skin contact can produce a slight burn.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 99
2. Boiling point (760 mm Hg): 57.3 C (135 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of 1,1-dichloroethane): 3.4
5. Melting point: -96.7 C (-142 F)
6. Vapor pressure at 20 C (68 F): 182 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.1
8. Evaporation rate (butyl acetate = 1): 11.6

• Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong caustics will cause formation of flammable and toxic acetaldehyde gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as vinyl chloride, hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,1-dichloroethane.
4. Special precautions: 1,1-Dichloroethane will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: -8.5 C (17 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 5.9; Upper: 15.9
4. Extinguishant: Foam, dry chemical, carbon dioxide

• Warning properties

The AIHA *Hygienic Guide* reports that 1,1-dichloroethane has a distinctive, easily recognizable odor at the TLV.

1,1-Dichloroethane is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based

on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,1-dichloroethane may be used. An analytical method for 1,1-dichloroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,1-dichloroethane.
- Clothing wet with liquid 1,1-dichloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1-dichloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1-dichloroethane, the person performing the operation should be informed of 1,1-dichloroethane's hazardous properties.
- Any clothing which becomes wet with liquid 1,1-dichloroethane should be removed immediately and not

of above 8,000 ppm for up to 7 hours were pathologic changes in the kidney and liver, and at much higher concentrations, near 64,000 ppm, damage to the lungs as well. Repeated daily exposure of several species of animals to 1,000 ppm resulted in no pathologic or hematologic changes. The liquid applied to the intact or abraded skin of rabbits produced slight edema and very slight necrosis after six daily applications. Instilled in the eyes of rabbits there was immediate, moderate conjunctival irritation and swelling which subsided within a week. There have been no reported cases of human overexposure by inhalation; prolonged, confined, or repeated skin contact can produce a slight burn.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 99
2. Boiling point (760 mm Hg): 57.3 C (135 F)
3. Specific gravity (water = 1): 1.2
4. Vapor density (air = 1 at boiling point of 1,1-dichloroethane): 3.4
5. Melting point: -96.7 C (-142 F)
6. Vapor pressure at 20 C (68 F): 182 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Less than 0.1
8. Evaporation rate (butyl acetate = 1): 11.6

• Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with strong caustics will cause formation of flammable and toxic acetaldehyde gas.
3. Hazardous decomposition products: Toxic gases and vapors (such as vinyl chloride, hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,1-dichloroethane.
4. Special precautions: 1,1-Dichloroethane will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: -3.5 C (17 F) (closed cup)
2. Autoignition temperature: Data not available
3. Flammable limits in air, % by volume: Lower: 5.9; Upper: 15.9
4. Extinguishant: Foam, dry chemical, carbon dioxide

• Warning properties

The AIHA *Hygienic Guide* reports that 1,1-dichloroethane has a distinctive, easily recognizable odor at the TLV.

1,1-Dichloroethane is not known to be an eye irritant.

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on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

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PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,1-dichloroethane.

- Clothing wet with liquid 1,1-dichloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1-dichloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1-dichloroethane, the person performing the operation should be informed of 1,1-dichloroethane's hazardous properties.

- Any clothing which becomes wet with liquid 1,1-dichloroethane should be removed immediately and not

reworn until the 1,1-dichloroethane is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid 1,1-dichloroethane may contact the eyes.

SANITATION

- Skin that becomes wet with liquid 1,1-dichloroethane should be immediately washed or showered with soap or mild detergent and water to remove any 1,1-dichloroethane.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1-dichloroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use as dewaxer of mineral oils; extractant for heat-sensitive substances	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a fumigant	General dilution ventilation of work area; personal protective equipment
Use in manufacture of vinyl chloride by vapor phase cracking; use in manufacture of high vacuum rubber and silicon grease; use as a chemical intermediate	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If 1,1-dichloroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If 1,1-dichloroethane gets on the skin, promptly flush the contaminated skin using soap or mild detergent and water. If 1,1-dichloroethane soaks through the clothing, remove the clothing immediately and flush the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of 1,1-dichloroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.

Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When 1,1-dichloroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If 1,1-dichloroethane is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. 1,1-Dichloroethane should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of 1,1-dichloroethane vapors are permitted.

- Waste disposal method:

1,1-Dichloroethane may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "1,1-Dichloroethane (Ethylidene Chloride)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

RESPIRATORY PROTECTION FOR 1,1-DICHLOROETHANE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
4000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 4000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for 1,2-Dichloroethylene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $\text{ClCH}=\text{CHCl}$
- Synonyms: Acetylene dichloride; dioform; trans-acetylene dichloride; sym-dichloroethylene
- Appearance and odor: Colorless liquid with an ether-like, slightly acrid odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,2-dichloroethylene is 200 parts of 1,2-dichloroethylene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 790 milligrams of 1,2-dichloroethylene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

1,2-Dichloroethylene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

• Effects of overexposure

Exposure to 1,2-dichloroethylene may cause dizziness, drowsiness, and unconsciousness.

• Reporting signs and symptoms

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,2-dichloroethylene.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to 1,2-dichloroethylene at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,2-dichloroethylene exposure.

—Liver disease: Although 1,2-dichloroethylene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of 1,2-dichloroethylene might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

1,2-Dichloroethylene vapor is a narcotic and a mucous-membrane irritant. Variations in toxicity of the cis- as compared with the trans-form have been reported. A concentration of 39,000 ppm was lethal to guinea pigs, and narcosis was produced at 18,000 ppm. Dogs exposed to high concentrations of vapor developed superficial corneal turbidity which was reversible. No effects were observed in several species with repeated exposure for up to 6 months at 1000 ppm. It has been used as a general anesthetic in man; one industrial fatality was due to very high vapor inhalation in a small enclosure.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 96.9
2. Boiling point (760 mm Hg): 45 to 60 C (113 to 140 F)
3. Specific gravity (water = 1): 1.27
4. Vapor density (air = 1 at boiling point of 1,2-dichloroethylene): 3.34
5. Melting point: -49 to -81.5 C (-56 to -115 F)
6. Vapor pressure at 20 C (68 F): 180 to 265 mm Hg

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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1,2-Dichloroethylene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.
- **Effects of overexposure**
Exposure to 1,2-dichloroethylene may cause dizziness, drowsiness, and unconsciousness.
- **Reporting signs and symptoms**
A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,2-dichloroethylene.
- **Recommended medical surveillance**
The following medical procedures should be made available to each employee who is exposed to 1,2-dichloroethylene at potentially hazardous levels:

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7. Solubility in water, g/100 g water at 20 C (68 F): 0.35 to 0.63

8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,2-dichloroethylene.

4. Special precautions: 1,2-Dichloroethylene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 2.2 to 3.9 C (36 to 39 F) (closed cup)
2. Autoignition temperature: 460 C (860 F) for trans-1,2-dichloroethylene

3. Flammable limits in air, % by volume: Lower: 9.7; Upper: 12.8

4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

May reports an odor threshold of 0.085 ppm for dichloroethylene. For the purposes of this guideline, 1,2-dichloroethylene is treated as a material with adequate warning properties.

1,2-Dichloroethylene is an eye irritant, according to Grant, but the concentrations at which irritation occurs are not mentioned.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

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- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,2-dichloroethylene.

- Clothing wet with liquid 1,2-dichloroethylene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,2-dichloroethylene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,2-dichloroethylene, the person performing the operation should be informed of 1,2-dichloroethylene's hazardous properties.

- Any clothing which becomes wet with liquid 1,2-dichloroethylene should be removed immediately and not reworn until the 1,2-dichloroethylene is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid 1,2-dichloroethylene may contact the eyes.

SANITATION

- Skin that becomes wet with liquid 1,2-dichloroethylene should be promptly washed or showered with soap or mild detergent and water to remove any 1,2-dichloroethylene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,2-dichloroethylene may occur and control methods which may be effective in each case:

7. Solubility in water, g/100 g water at 20 C (68 F): 0.35 to 0.63

8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,2-dichloroethylene.

4. Special precautions: 1,2-Dichloroethylene will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: 2.2 to 3.9 C (36 to 39 F) (closed cup)
2. Autoignition temperature: 460 C (860 F) for trans-1,2-dichloroethylene

3. Flammable limits in air, % by volume: Lower: 9.7; Upper: 12.8

4. Extinguishant: Dry chemical, foam, carbon dioxide

- **Warning properties**

May reports an odor threshold of 0.085 ppm for dichloroethylene. For the purposes of this guideline, 1,2-dichloroethylene is treated as a material with adequate warning properties.

1,2-Dichloroethylene is an eye irritant, according to Grant, but the concentrations at which irritation occurs are not mentioned.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of 1,2-dichloroethylene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,2-dichloroethylene may be used. An analytical method for 1,2-dichloroethylene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,2-dichloroethylene.

- Clothing wet with liquid 1,2-dichloroethylene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,2-dichloroethylene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,2-dichloroethylene, the person performing the operation should be informed of 1,2-dichloroethylene's hazardous properties.

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SANITATION

- Skin that becomes wet with liquid 1,2-dichloroethylene should be promptly washed or showered with soap or mild detergent and water to remove any 1,2-dichloroethylene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,2-dichloroethylene may occur and control methods which may be effective in each case:

Operation	Controls
Use as a low-temperature solvent for heat-sensitive substances in extraction of caffeine, perfume oils, and fats from flesh of animals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber and dye industries in extraction and application	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a direct solvent in gums, waxes, oils, camphor, and phenol; use in solvent mixtures for esters and ether derivatives, lacquers, resins, thermoplastics, and artificial fibers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in organic synthesis for polymers and telomers	Process enclosure; local exhaust ventilation; personal protective equipment
Use in miscellaneous applications as liquid dry cleaning agent, cleaning solution for printed circuit boards, food packaging adhesives, and germicidal fumigants	General dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If 1,2-dichloroethylene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If 1,2-dichloroethylene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,2-dichloroethylene soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of 1,2-dichloroethylene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.

Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When 1,2-dichloroethylene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If 1,2-dichloroethylene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. 1,2-Dichloroethylene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of 1,2-dichloroethylene vapors are permitted.

• Waste disposal method:

1,2-Dichloroethylene may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

Operation	Controls
Use as a low-temperature solvent for heat-sensitive substances in extraction of caffeine, perfume oils, and fats from flesh of animals	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in rubber and dye industries in extraction and application	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a direct solvent in gums, waxes, oils, camphor, and phenol; use in solvent mixtures for esters and ether derivatives, lacquers, resins, thermoplastics, and artificial fibers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
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REFERENCES

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RESPIRATORY PROTECTION FOR 1,2-DICHLOROETHYLENE

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
4000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 4000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Propylene Dichloride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $\text{CH}_3\text{CHClCH}_2\text{Cl}$
- Synonyms: 1,2-Dichloropropane
- Appearance and odor: Colorless liquid with an odor like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for propylene dichloride is 75 parts of propylene dichloride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 350 milligrams of propylene dichloride per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

Propylene dichloride can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed.

• Effects of overexposure

1. **Short-term Exposure:** Overexposure to propylene dichloride causes eye and skin irritation and may cause drowsiness or lightheadedness.
2. **Long-term Exposure:** Prolonged overexposure to propylene dichloride may affect the liver and kidneys.
3. **Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to propylene dichloride.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to propylene dichloride at potentially hazardous levels:

1. **Initial Medical Screening:** Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from propylene dichloride exposure.

—Skin disease: Propylene dichloride can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Propylene dichloride is known as a liver toxin in animals and justifies consideration before exposing persons with impaired liver function.

—Kidney disease: Propylene dichloride is known as a kidney toxin in animals and justifies special consideration before exposing persons with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of propylene dichloride might cause exacerbation of symptoms due to its irritant properties.

2. **Periodic Medical Examination:** Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

Propylene dichloride vapor is a narcotic and an eye irritant. At 2200 ppm for 7 hours, guinea pigs developed severe conjunctival swelling, as well as signs of respiratory irritation and incoordination; some died after 5 daily exposures, showing severe liver injury, some kidney injury, and occasional adrenal changes. Repeated inhalation of 1000 ppm caused some deaths among dogs after 24 exposures of 7 hours' duration, and among rats after only 7 exposures. There was early onset of lacrimation, eye irritation, and incoordination. Liver damage was the main finding in the animals that died. At 400 ppm, rats and guinea pigs exposed for up to 140

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
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daily 7-hour exposures showed no ill effects and no histologic changes. However, of a group of C3H-strain mice exposed at 400 ppm, some died; others developed hepatomas, a finding of equivocal significance. Propylene dichloride is mildly irritating to human skin, and some skin absorption may occur from exposure to the liquid. The undiluted liquid is moderately irritating to the eyes but does not cause permanent injury.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 113
2. Boiling point (760 mm Hg): 96.1 C (205 F)
3. Specific gravity (water = 1): 1.16
4. Vapor density (air = 1 at boiling point of propylene dichloride): 3.9
5. Melting point: -100 C (-148 F)
6. Vapor pressure at 20 C (68 F): 39.5 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.26
8. Evaporation rate (butyl acetate = 1): Greater than 1

• Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Strong acids may cause decomposition.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide and hydrogen chloride) may be released in a fire involving propylene dichloride.
4. Special precautions: Propylene dichloride will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: 15.6 C (60 F) (closed cup)
2. Autoignition temperature: 557 C (1035 F)
3. Flammable limits in air, % by volume (at 100 C): Lower: 3.4; Upper: 14.5
4. Extinguishant: Dry chemical, foam, carbon dioxide

• Warning properties

1. Odor Threshold: May reports an odor threshold of 50 ppm. The AIHA *Hygienic Guide* states that "human subjects described the odor as 'strong' at 130 to 190 ppm and 'not noticeable' at 15 to 23 ppm."
2. Eye Irritation Level: According to Grant, "exposure of guinea pigs to 2200 ppm in air for many hours until most were dead caused lacrimation and swelling of the lids and conjunctiva. To the extent that the corneas were left unprotected, bluish discoloration of the corneas and infection developed. Rabbits exposed to the same conditions showed little irritation." No quantitative information is available concerning the threshold of eye irritation. No ill effects have been observed in animals chronically exposed to 400 ppm.
3. Evaluation of Warning Properties: Since the odor threshold of propylene dichloride is below the permissible exposure limit, this substance is treated as a material

with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of propylene dichloride vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure propylene dichloride may be used. An analytical method for propylene dichloride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6). PB 265 026).

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1. Odor Threshold: May reports an odor threshold of 50 ppm. The *AIHA Hygienic Guide* states that "human subjects described the odor as 'strong' at 130 to 190 ppm and 'not noticeable' at 15 to 23 ppm."

2. Eye Irritation Level: According to Grant, "exposure of guinea pigs to 2200 ppm in air for many hours until most were dead caused lacrimation and swelling of the lids and conjunctiva. To the extent that the corneas were left unprotected, bluish discoloration of the corneas and infection developed. Rabbits exposed to the same conditions showed little irritation." No quantitative information is available concerning the threshold of eye irritation. No ill effects have been observed in animals chronically exposed to 400 ppm.

3. Evaluation of Warning Properties: Since the odor threshold of propylene dichloride is below the permissible exposure limit, this substance is treated as a material

with adequate warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of propylene dichloride vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure propylene dichloride may be used. An analytical method for propylene dichloride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6). PB 265 026).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid propylene dichloride.

• Clothing wet with liquid propylene dichloride should be placed in closed containers for storage until it can be

discarded or until provision is made for the removal of propylene dichloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the propylene dichloride, the person performing the operation should be informed of propylene dichloride's hazardous properties.

- Any clothing which becomes wet with liquid propylene dichloride should be removed immediately and not reworn until the propylene dichloride is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid propylene dichloride may contact the eyes.

SANITATION

- Skin that becomes wet with liquid propylene dichloride should be promptly washed or showered with soap or mild detergent and water to remove any propylene dichloride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to propylene dichloride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a soil fumigant for protection of fruit and nut crops, field crops, beets, and tobacco against nematodes	Adequate ventilation; personal protective equipment
Use in cleaning, degreasing, and spot removal operations including paint and varnish removal	Local exhaust ventilation; personal protective equipment
Use during rubber compounding and vulcanizing operations	Local exhaust ventilation; personal protective equipment
Use during extraction processing of fats, oils, lactic acid, and petroleum waxes	Local exhaust ventilation; personal protective equipment
Use in the manufacture of tetrachloroethylene and propylene oxide	Local exhaust ventilation; personal protective equipment
Use as an additive and lead scavenger in antiknock fluids	Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If propylene dichloride gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If propylene dichloride gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If propylene dichloride soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of propylene dichloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When propylene dichloride has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If propylene dichloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Propylene dichloride should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal method:

discarded or until provision is made for the removal of propylene dichloride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the propylene dichloride, the person performing the operation should be informed of propylene dichloride's hazardous properties.

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RESPIRATORY PROTECTION FOR PROPYLENE DICHLORIDE

Condition	Minimum Respiratory Protection* Required Above 75 ppm
Vapor Concentration	
400 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Ethyl Benzene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_2H_5C_6H_5$
- Synonyms: Phenylethane; ethylbenzol
- Appearance and odor: Colorless liquid with an aromatic odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ethyl benzene is 100 parts of ethyl benzene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 435 milligrams of ethyl benzene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

Ethyl benzene can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

• Effects of overexposure

1. *Short-term Exposure:* Ethyl benzene causes irritation of the eyes, nose, throat, and skin. With exposure to high concentrations, irritating effects are more pronounced, and a person may begin to feel weak, dizzy, drowsy, and become unconscious.

2. *Long-term Exposure:* Prolonged or repeated ethyl benzene exposure of the skin may cause skin rash.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ethyl benzene.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to ethyl benzene at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from ethyl benzene exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of ethyl benzene might cause exacerbation of symptoms due to its irritant properties or psychic reflex bronchospasm.

—Kidney disease: Although ethyl benzene is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with possible impairment of renal function.

—Liver disease: Although ethyl benzene is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Skin disease: Ethyl benzene is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

Ethyl benzene is primarily an irritant of skin and, to some degree, of eyes and upper respiratory tract. Systemic absorption causes depression of the central nervous system with narcosis at very high concentrations. Aspiration of small amounts causes extensive edema and hemorrhage of lung tissue. It is readily metabolized and excreted chiefly as mandelic acid in the urine.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
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CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 106
2. Boiling point (760 mm Hg): 136 C (277 F)
3. Specific gravity (water = 1): 0.865
4. Vapor density (air = 1 at boiling point of ethyl benzene): 3.66
5. Melting point: -95 C (-139 F)
6. Vapor pressure at 20 C (68 F): 7.1 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.015
8. Evaporation rate (butyl acetate = 1): Less than 1

- **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving ethyl benzene.

4. Special precautions: None

- **Flammability**

1. Flash point: 15 C (59 F) (closed cup)
2. Autoignition temperature: 432 C (810 F)
3. Flammable limits in air, % by volume: Lower: 1.0; Upper: 6.7
4. Extinguishant: Dry chemical, foam, or carbon dioxide

- **Warning properties**

1. Odor Threshold: According to the Department of Transportation's *CHRIS Hazardous Chemical Data*, ethyl benzene has an odor threshold of 140 ppm.

2. Eye Irritation Level: According to the AIHA *Hygienic Guide*, "the vapor caused a noticeable eye irritation in humans at concentrations of 200 ppm."

3. Evaluation of Warning Properties: Through its odor and irritant effects, ethyl benzene can be detected at a concentration less than twice the permissible exposure limit. Therefore, for the purposes of this guideline, ethyl benzene is treated as a material with adequate warning properties.

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Sampling and analyses may be performed by collection of ethyl benzene vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified

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• Employees should be provided with and required to use splash-proof safety goggles where liquid ethyl benzene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid ethyl benzene should be promptly washed or showered with soap or mild detergent and water to remove any ethyl benzene.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ethyl benzene may occur and control methods which may be effective in each case:

Operation	Controls
Liberation during manufacture of styrene monomer	Local exhaust ventilation
Use during spray application of vinyl resin surface coating	Local exhaust ventilation; personal protective equipment
Liberation during manufacture of paints, varnishes, and other surface coatings	Local exhaust ventilation; general dilution ventilation
Use in manufacture and application of rubber adhesives	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use during electroplating of aluminum on copper or steel	Local exhaust ventilation for open-surface tanks
Liberation during oven baking and drying of surface coatings	Local exhaust ventilation for ovens
Liberation during application of surface coatings by dipping, flow coatings, and roller coating	Local exhaust ventilation
Liberation during use as an intermediate in dye manufacture	General dilution ventilation
Use as a heat-transfer medium; use as a dielectric	General dilution ventilation; personal protective equipment
Liberation during production of acetophenone by oxidation of ethyl benzene	General dilution ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If ethyl benzene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention as soon as possible. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If ethyl benzene gets on the skin, promptly flush the contaminated skin with water. If ethyl benzene soaks through the clothing, remove the clothing immediately and flush the skin with water. When there is skin irritation, get medical attention.

• Breathing

If a person breathes in large amounts of ethyl benzene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

If ethyl benzene has been swallowed, do not induce vomiting. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If ethyl benzene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid. Ethyl benzene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

- Waste disposal methods:

Ethyl benzene may be disposed of:

1. By absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

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REFERENCES

- American Conference of Governmental Industrial Hygienists: "Ethyl Benzene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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RESPIRATORY PROTECTION FOR ETHYL BENZENE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

2. By atomizing in a suitable combustion chamber. Combustion may be improved by mixing with a more flammable liquid.

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Occupational Health Guideline for Methylene Chloride

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: CH_2Cl_2
- Synonyms: Dichloromethane; methylene dichloride
- Appearance and odor: Colorless liquid with an odor like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylene chloride is 500 parts of methylene chloride per million parts of air (ppm) averaged over an eight-hour work shift, with an acceptable ceiling level of 1000 ppm and a maximum peak concentration of 2000 ppm for 5 minutes in any two-hour period. NIOSH has recommended that the permissible exposure limit be reduced to 75 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 500 ppm averaged over a 15-minute period. NIOSH further recommends that permissible levels of methylene chloride be reduced where carbon monoxide is present. The NIOSH Criteria Document for Methylene Chloride should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Methylene chloride can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

• Effects of overexposure

1. *Short-term Exposure:* Methylene chloride is an anesthetic. Inhaling the vapor may cause mental confusion,

light-headedness, nausea, vomiting, and headache. Continued exposure may cause increased light-headedness, staggering, unconsciousness, and death. High vapor concentrations may also cause irritation of the eyes and respiratory tract. Exposure to this chemical may make the symptoms of angina worse. Skin exposure to the liquid may cause irritation. If the liquid is held in contact with the skin, it may cause skin burns. Splashes of the liquid into the eyes may cause irritation.

2. *Long-term Exposure:* Prolonged or repeated exposure to methylene chloride may cause irritation of the skin.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylene chloride.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to methylene chloride at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the employee at increased risk, and to establish a baseline for future health monitoring. Examination of the skin, liver, kidneys, cardiovascular system, and blood should be stressed. Clinical impressions of the autonomic nervous system and pulmonary function should be made, with additional tests conducted where indicated.

—Skin disease: Methylene chloride can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver function test: Methylene chloride causes liver damage in animals and this justifies consideration before exposing persons with impaired liver function. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Kidney disease: Methylene chloride causes kidney damage in animals and this justifies special considera-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
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tion before exposing persons with impaired renal function.

—Cardiovascular disease: Because of reports of excessive carbon monoxide levels following exposure to methylene chloride, persons with cardiac disease may be at increased risk.

—A complete blood count: A complete blood count should be performed, including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit. Carboxyhemoglobin values should also be determined periodically, and any level above 5% should prompt an investigation of the worker and his workplace.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

Methylene chloride vapor is a mild narcotic. Exposure of animals to 15,000 ppm for 7 hours was fatal. Animal experiments have shown that continuous exposure to 1,000 ppm can be lethal in 5 to 7 weeks for dogs and that fatty livers, icterus, pneumonia, and splenic atrophy developed in dogs. Cardiac arrhythmias attributed to sensitization of the myocardium have been observed following exposure to high concentrations of some chlorinated hydrocarbons, but dogs exposed to 10,000 and 20,000 ppm of methylene chloride did not show this phenomenon. In human experiments, inhalation of 500 to 1000 ppm for 1 to 2 hours resulted in lightheadedness; there was sustained elevation of carboxyhemoglobin level. High exposures have resulted in deaths in industrial situations. Lower but unknown concentrations have caused such symptoms as lightheadedness, weakness, nausea, and "drunken behavior," resulting in mistakes and accidental falls. Phosgene poisoning has been reported to occur in several cases where methylene chloride was used in the presence of an open fire. Liquid methylene chloride is irritating to the skin on repeated contact. Splashed in the eye, it is painfully irritating, but is not likely to cause serious injury.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 84.9
2. Boiling point (760 mm Hg): 39.8 C (104 F)
3. Specific gravity (water = 1): 1.3
4. Vapor density (air = 1 at boiling point of methylene chloride): 2.9
5. Melting point: -97 C (-142 F)
6. Vapor pressure at 20 C (68 F): 350 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 1.32
8. Evaporation rate (butyl acetate = 1): 27.5

• **Reactivity**

1. Conditions contributing to instability: Heat and moisture
2. Incompatibilities: Contact with strong oxidizers, strong caustics, and chemically active metals such as

aluminum or magnesium powder, sodium and potassium may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving methylene chloride.

4. Special precautions: Liquid methylene chloride will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: None with normal test method
2. Autoignition temperature: 556 C (1033 F)
3. Flammable limits in air, % by volume: (at elevated temperatures) Lower: 12; Upper: 19
4. Extinguishant: Dry chemical, carbon dioxide, foam

• **Warning properties**

1. Odor Threshold: Different authors have reported varying odor thresholds for methylene chloride. Summer and May both report 150 ppm; Kirk-Othmer and Sax both report 25 to 50 ppm; Spector reports 320 ppm. Patty, however, states that since one can become adapted to the odor, it cannot be considered an adequate warning property.

2. Eye Irritation Level: Grant reports that methylene chloride "presents no particular hazard to the eyes." Kirk-Othmer, however, reports that "methylene chloride vapor is seriously damaging to the eyes." Sax agrees with Kirk-Othmer's statement.

The *Documentation of TLVs* states that irritation of the eyes has been observed in workers who had been exposed to concentrations up to 5000 ppm, but that neurasthenic disorders were found in 50% and digestive disturbances in 30% of the persons exposed.

3. Other Information: Gleason reports that methylene chloride may be "irritating to the respiratory tract and may produce pulmonary edema" but gives no quantitative information. The *Documentation of TLVs* reports that in one investigation, irritation of the respiratory passages was observed in workers who had been exposed to concentrations up to 5000 ppm.

4. Evaluation of Warning Properties: Since no detailed information is available relating the irritant effects of methylene chloride to air concentrations and since adaptation to the odor occurs, methylene chloride is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

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• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methylene chloride. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Peak Above Ceiling Evaluation

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of methylene chloride. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylene chloride may be used. An analytical method for methylene chloride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylene chloride.

• Non-impervious clothing which becomes wet with liquid methylene chloride should be removed promptly and not reworn until the methylene chloride is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methylene chloride may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methylene chloride should be promptly washed or showered with soap or mild detergent and water to remove any methylene chloride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylene chloride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in paint and varnish removers; manufacture of aerosols; cold cleaning and ultrasonic cleaning; and as an extraction solvent for foods and furniture processing	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a cooling solvent in manufacture of cellulose acetate; in organic synthesis; and in plastics processing	Process enclosure; local exhaust ventilation
Use as a solvent in vapor degreasing of thermal switches and thermometers	Process enclosure; local exhaust ventilation
Use as a secondary refrigerant in air conditioning and scientific testing	General dilution ventilation; local exhaust ventilation; personal protective equipment

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of methylene chloride. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of methylene chloride. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylene chloride may be used. An analytical method for methylene chloride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylene chloride.

- Non-impervious clothing which becomes wet with liquid methylene chloride should be removed promptly and not reworn until the methylene chloride is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid methylene chloride may contact the eyes.

SANITATION

- Skin that becomes wet with liquid methylene chloride should be promptly washed or showered with soap or mild detergent and water to remove any methylene chloride.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylene chloride may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in paint and varnish removers; manufacture of aerosols; cold cleaning and ultrasonic cleaning; and as an extraction solvent for foods and furniture processing	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a cooling solvent in manufacture of cellulose acetate; in organic synthesis; and in plastics processing	Process enclosure; local exhaust ventilation
Use as a solvent in vapor degreasing of thermal switches and thermometers	Process enclosure; local exhaust ventilation
Use as a secondary refrigerant in air conditioning and scientific testing	General dilution ventilation; local exhaust ventilation; personal protective equipment

Operation

Use as an extraction solvent for edible fats, coca, butter, beer flavoring in hops, decaffeinated coffee, oleoresin manufacture, oils, waxes, perfumes, flavorings, and drugs

Use as a solvent for paints, lacquers, varnishes, enamels, adhesives, rubber cements, manufacture of printed circuit boards, as a carrier for pharmaceutical tablet coatings, shrink-fitting of synthetic rubber covers, and dyeing of synthetic fibers

Controls

General dilution ventilation; local exhaust ventilation; personal protective equipment

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EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If methylene chloride gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If methylene chloride gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water if the methylene chloride has not already evaporated. If methylene chloride soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of methylene chloride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When methylene chloride has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If methylene chloride is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Methylene Chloride," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard . . . Occupational Exposure to Methylene Chloride*, HEW Publication No. (NIOSH) 76-138, GPO No. 017-033-00194-4, U.S. Government Printing Office, Washington, D.C., 1976.

Operation	Controls
Use as an extraction solvent for edible fats, coca, butter, beer flavoring in hops, decaffeinated coffee, oleoresin manufacture, oils, waxes, perfumes, flavorings, and drugs	General dilution ventilation; local exhaust ventilation; personal protective equipment
Use as a solvent for paints, lacquers, varnishes, enamels, adhesives, rubber cements, manufacture of printed circuit boards, as a carrier for pharmaceutical tablet coatings, shrink-fitting of synthetic rubber covers, and dyeing of synthetic fibers	General dilution ventilation; local exhaust ventilation; personal protective equipment

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RESPIRATORY PROTECTION FOR METHYLENE CHLORIDE

Condition	Minimum Respiratory Protection* Required Above 500 ppm
Vapor Concentration	
5000 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 5000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Naphthalene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_{10}H_8$
- Synonyms: White tar; naphthalin
- Appearance and odor: Colorless to brown solid with the odor of mothballs.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for naphthalene is 10 parts of naphthalene per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 50 milligrams of naphthalene per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

Naphthalene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

• Effects of overexposure

1. *Short-term Exposure:* Inhalation or ingestion of naphthalene may cause abdominal cramps, nausea, vomiting, diarrhea, headache, tiredness, confusion, painful urination, and bloody or dark urine. Swallowing large amounts may cause convulsions or coma. Inhalation, ingestion, and possibly skin absorption of naphthalene may cause destruction of red blood cells with anemia, fever, yellow jaundice, bloody urine, kidney and liver damage. Naphthalene, on contact with the eyes, has produced irritation. Naphthalene, on contact with the skin, has produced skin irritation.

2. *Long-term Exposure:* Repeated skin exposure to naphthalene may cause an allergic rash. Repeated exposure may cause cataracts.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to naphthalene.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to naphthalene at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a deficiency of glucose-6-phosphate dehydrogenase in erythrocytes may be at increased risk from exposure. Examination of the eyes, blood, liver and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Naphthalene has been shown to cause red blood cell hemolysis. A complete blood count should be performed, including a red cell count, a white cell count, and a differential count of a stained smear, as well as hemoglobin and hematocrit.

—Urinalysis: Since kidney damage may also occur from exposure to naphthalene, a urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

• Summary of toxicology

Naphthalene vapor causes hemolysis and eye irritation; it may cause cataracts. Severe intoxication from ingestion of the solid results in characteristic manifestations of marked intravascular hemolysis and its consequences, including potentially fatal hyperkalemia. Initial symptoms include eye irritation, headache, confu-

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 128.2
2. Boiling point (760 mm Hg): 218 C (424 F)
3. Specific gravity (water = 1): 1.14
4. Vapor density (air = 1 at boiling point of naphthalene): 4.4
5. Melting point: 74–80 C (165–176 F)
6. Vapor pressure at 20 C (68 F): 0.05 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.003
8. Evaporation rate (butyl acetate = 1): Much less than 1

• Reactivity

1. Conditions contributing to instability: None.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as dense acrid smoke and carbon monoxide) may be released in a fire involving naphthalene.
4. Special precautions: Melted naphthalene will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: 79 C (174 F) (closed cup)
2. Autoignition temperature: 526 C (979 F)
3. Flammable limits in air, % by volume: Lower: 0.9; Upper: 5.9
4. Extinguishant: Carbon dioxide, dry chemical, foam

• Warning properties

1. Odor Threshold: The AIHA *Hygienic Guide* reports that the odor threshold of naphthalene is "at least as low as 0.3 ppm."

2. Eye Irritation Level: The *Hygienic Guide* states that "naphthalene vapor is reported to cause eye irritation at 15 ppm or above in air."

3. Evaluation of Warning Properties: Through its odor and irritant effects, naphthalene can be detected at or below the permissible exposure limit. Naphthalene, therefore, is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure naphthalene may be used. An analytical method for naphthalene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

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Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure naphthalene may be used. An analytical method for naphthalene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 4, 1978, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00317-3).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with naphthalene or liquids containing naphthalene.
- If employees' clothing may have become contaminated with solid naphthalene, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with naphthalene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of naphthalene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the naphthalene, the person performing the operation should be informed of naphthalene's hazardous properties.
- Non-impervious clothing which becomes contaminated with naphthalene should be removed promptly and not reworn until the naphthalene is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where solid naphthalene or liquids containing naphthalene may contact the eyes.

SANITATION

- Skin that becomes contaminated with naphthalene should be promptly washed or showered with soap or mild detergent and water to remove any naphthalene.
- Eating and smoking should not be permitted in areas where solid naphthalene is handled, processed, or stored.
- Employees who handle naphthalene or liquids containing naphthalene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to naphthalene may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of insecticide and moth repellant as flakes, powder, balls, or cakes	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use as a fumigant for moth repellant and insecticide	General dilution ventilation; personal protective equipment

Operation

Use in manufacture of chemical intermediates for production of pharmaceuticals, resins, dyes, plasticizers, solvents, coatings, insecticides, pigments, rubber chemicals, tanning agents, surfactants, waxes, cable coatings, textile spinning lubricants, rodenticides, and in storage batteries

Manufacture of naphthalene

Controls

Local exhaust ventilation; general dilution ventilation; personal protective equipment

Local exhaust ventilation; process enclosure; general dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If naphthalene or liquids containing naphthalene get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If molten naphthalene gets on the skin, immediately flush the skin with large amounts of water. Get medical attention immediately. If naphthalene or liquids containing naphthalene get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If naphthalene or liquids containing naphthalene penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of naphthalene, move the exposed person to fresh air at once.

• Swallowing

When naphthalene has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify some-

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• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify some-

one else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.
- If naphthalene is spilled, the following steps should be taken:
 1. Ventilate area of spill.
 2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber.
- Waste disposal methods:
Naphthalene may be disposed of:
 1. By making packages of naphthalene in paper or other flammable material and burning in a suitable combustion chamber.
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ADDITIONAL INFORMATION

To find additional information on naphthalene, look up naphthalene in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Naphthalene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Naphthalene," *Hygienic Guide Series*, Detroit, Michigan, 1967.
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RESPIRATORY PROTECTION FOR NAPHTHALENE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Particulate and Vapor Concentration	
500 ppm or less	<p>A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust filter.</p> <p>A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust filter.</p> <p>Any supplied-air respirator with a full facepiece, helmet, or hood.</p> <p>Any self-contained breathing apparatus with a full facepiece.</p>
Greater than 500 ppm or entry and escape from unknown concentrations	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p> <p>A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.</p>
Fire Fighting	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p>
Escape	<p>Any gas mask providing protection against organic vapors and particulates.</p> <p>Any escape self-contained breathing apparatus.</p>
*Only NIOSH-approved or MSHA-approved equipment should be used.	

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Occupational Health Guideline for Phenol

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: C_6H_5OH
- Synonyms: Carboic acid; monohydroxybenzene
- Appearance and odor: Colorless to pink solid or thick liquid with a characteristic, sweet, tarry odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phenol is 5 parts of phenol per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 19 milligrams of phenol per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be changed to 20 mg/m^3 averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling of 60 mg/m^3 averaged over a 15-minute period. The NIOSH Criteria Document for Phenol should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Phenol can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

• Effects of overexposure

1. Short-term Exposure: Phenol has a marked corrosive effect on any tissue. When it comes in contact with the eyes, it may cause severe damage and blindness. On contact with the skin, it does not cause pain but causes a whitening of the exposed area. If the chemical is not removed promptly, it may cause a severe burn or

systemic poisoning. Systemic effects may occur from any route of exposure, especially after skin contact.

2. Long-term Exposure: Repeated or prolonged exposure to phenol may cause chronic phenol poisoning. The symptoms of chronic poisoning include vomiting, difficulty in swallowing, diarrhea, lack of appetite, headache, fainting, dizziness, dark urine, mental disturbances, and possibly a skin rash. Liver damage and discoloration of the skin may occur.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phenol.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to phenol at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Persons with a history of convulsive disorders or abnormalities of the skin, respiratory tract, liver, or kidneys would be expected to be at increased risk from exposure. Examination of the liver, kidneys, and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Darkening of the urine has occurred in persons exposed to phenol after accidental ingestion or skin contact. A urinalysis should be performed, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. Urinary phenol is useful if good individual background levels are available.

—Liver function tests: Since liver damage has been observed in humans exposed to phenol, a profile of liver function should be performed by using a medically acceptable array of biochemical tests.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
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2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

Phenol in the vapor form or in solution is an irritant to the eyes, mucous membranes, and skin; systemic absorption causes central nervous system effects as well as liver and kidney damage. Sudden collapse is characteristic of gross overexposure. In animals, prolonged inhalation of the vapor at 30 to 60 ppm induced respiratory difficulty, lung damage, and paralysis. Systemic absorption by animals caused muscle twitching and severe convulsions. There are no reports of human fatalities from inhalation of the vapor, although one case of severe poisoning has been reported. Ingestion of lethal amounts (as little as 1 g) cause severe burns of the mouth and throat, marked abdominal pain, cyanosis, muscular weakness, collapse, coma, and death; tremors, convulsions, or muscle twitching were occasionally observed but were not severe. A laboratory technician repeatedly exposed to unknown vapor concentrations and liquid spilled on the skin developed anorexia, weight loss, weakness, muscle aches and pain, and dark urine; during several months of nonexposure there was gradual improvement in his condition, but after brief reexposure he suffered an immediate worsening of symptoms with prompt darkening of the urine and tender enlargement of the liver. Brief intermittent industrial exposures to vapor concentrations of 48 ppm of phenol (accompanied by 8 ppm of formaldehyde) caused marked irritation of eyes, nose, and throat. Concentrated phenol solutions are severely irritating to the human eye and cause conjunctival swelling; the cornea becomes white and hypesthetic; loss of vision has occurred in some cases. Solutions of phenol have a marked corrosive action on any tissue on contact; on skin, there is local anesthesia and a white discoloration, and the area may subsequently become gangrenous; severe dermatitis will result from contact with dilute solutions, and prolonged exposure may result in ochronosis. In workers making phenol-formaldehyde plastic, the urinary level of total phenol, free plus conjugated, was proportional to the air concentration of phenol up to 12.5 mg/m³ of workroom air. Mice were treated twice weekly for 72 weeks by application of 1 drop of a 10% solution of phenol in benzene to the shaved dorsal skin; after 52 weeks of treatment there were papillomas in 5 of 14 mice, and 1 fibrosarcoma appeared at 58 weeks.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 94.11
2. Boiling point (760 mm Hg): 182 C (359 F)
3. Specific gravity (water = 1): 1.07 (solid); 1.05 (liquid)
4. Vapor density (air = 1 at boiling point of phenol): 3.24

5. Melting point: 41 C (106 F)

6. Vapor pressure at 20 C (68 F): 0.36 mm Hg

7. Solubility in water, g/100 g water at 20 C (68 F): 8.4

8. Evaporation rate (butyl acetate = 1): Less than 0.01

• **Reactivity**

1. Conditions contributing to instability: Heat

2. Incompatibilities: Contact with strong oxidizers (especially calcium hypochlorite) may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving phenol.

4. Special precautions: Liquid phenol will attack some forms of plastics, rubber, and coatings. Hot liquid phenol will attack aluminum, magnesium, lead, and zinc metals.

• **Flammability**

1. Flash point: 79 C (174 F) (closed cup)

2. Autoignition temperature: 715 C (1319 F)

3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 8.6

4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

• **Warning properties**

1. Odor Threshold: Summer reports that the odor threshold of phenol is 3 ppm; the Manufacturing Chemists Association reports 0.3 ppm; Thienes and Haley report 5 ppm.

2. Irritation Levels: The *Documentation of TLVs* reports that intermittent exposures to 48 ppm phenol have been observed to produce eye, nose, and throat irritation. Formaldehyde was also present in this atmosphere at a concentration of 8 ppm. The Respirator Review Committee considers the source of the eye irritation to be the 8 ppm formaldehyde rather than the phenol.

3. Evaluation of Warning Properties: Since the odor threshold of phenol is at or below the permissible exposure limit, phenol is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of phenol. Each measurement

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

Phenol in the vapor form or in solution is an irritant to the eyes, mucous membranes, and skin; systemic absorption causes central nervous system effects as well as liver and kidney damage. Sudden collapse is characteristic of gross overexposure. In animals, prolonged inhalation of the vapor at 30 to 60 ppm induced respiratory difficulty, lung damage, and paralysis. Systemic absorption by animals caused muscle twitching and severe convulsions. There are no reports of human fatalities from inhalation of the vapor, although one case of severe poisoning has been reported. Ingestion of lethal amounts (as little as 1 g) cause severe burns of the mouth and throat, marked abdominal pain, cyanosis, muscular weakness, collapse, coma, and death; tremors, convulsions, or muscle twitching were occasionally observed but were not severe. A laboratory technician repeatedly exposed to unknown vapor concentrations and liquid spilled on the skin developed anorexia, weight loss, weakness, muscle aches and pain, and dark urine; during several months of nonexposure there was gradual improvement in his condition, but after brief reexposure he suffered an immediate worsening of symptoms with prompt darkening of the urine and tender enlargement of the liver. Brief intermittent industrial exposures to vapor concentrations of 48 ppm of phenol (accompanied by 8 ppm of formaldehyde) caused marked irritation of eyes, nose, and throat. Concentrated phenol solutions are severely irritating to the human eye and cause conjunctival swelling; the cornea becomes white and hypesthetic; loss of vision has occurred in some cases. Solutions of phenol have a marked corrosive action on any tissue on contact; on skin, there is local anesthesia and a white discoloration, and the area may subsequently become gangrenous; severe dermatitis will result from contact with dilute solutions, and prolonged exposure may result in ochronosis. In workers making phenol-formaldehyde plastic, the urinary level of total phenol, free plus conjugated, was proportional to the air concentration of phenol up to 12.5 mg/m³ of workroom air. Mice were treated twice weekly for 72 weeks by application of 1 drop of a 10% solution of phenol in benzene to the shaved dorsal skin; after 52 weeks of treatment there were papillomas in 5 of 14 mice, and 1 fibrosarcoma appeared at 58 weeks.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 94.11
2. Boiling point (760 mm Hg): 182 C (359 F)
3. Specific gravity (water = 1): 1.07 (solid); 1.05 (liquid)
4. Vapor density (air = 1 at boiling point of phenol): 3.24

5. Melting point: 41 C (106 F)
6. Vapor pressure at 20 C (68 F): 0.36 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 8.4
8. Evaporation rate (butyl acetate = 1): Less than 0.01

• **Reactivity**

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact with strong oxidizers (especially calcium hypochlorite) may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide) may be released in a fire involving phenol.
4. Special precautions: Liquid phenol will attack some forms of plastics, rubber, and coatings. Hot liquid phenol will attack aluminum, magnesium, lead, and zinc metals.

• **Flammability**

1. Flash point: 79 C (174 F) (closed cup)
2. Autoignition temperature: 715 C (1319 F)
3. Flammable limits in air, % by volume: Lower: 1.7; Upper: 8.6
4. Extinguishant: Alcohol foam, carbon dioxide, dry chemical

• **Warning properties**

1. Odor Threshold: Summer reports that the odor threshold of phenol is 3 ppm; the Manufacturing Chemists Association reports 0.3 ppm; Thienes and Haley report 5 ppm.
2. Irritation Levels: The *Documentation of TLVs* reports that intermittent exposures to 48 ppm phenol have been observed to produce eye, nose, and throat irritation. Formaldehyde was also present in this atmosphere at a concentration of 8 ppm. The Respirator Review Committee considers the source of the eye irritation to be the 8 ppm formaldehyde rather than the phenol.
3. Evaluation of Warning Properties: Since the odor threshold of phenol is at or below the permissible exposure limit, phenol is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of phenol. Each measurement

should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of phenol in a bubbler containing sodium hydroxide, followed by treatment with sulfuric acid, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure phenol may be used. An analytical method for phenol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid or liquid phenol or liquids containing phenol.
- If employees' clothing has had any possibility of being contaminated with solid or liquid phenol or liquids containing phenol, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with solid or liquid phenol or liquids containing phenol should be placed in closed containers for storage until it can be discarded or until provision is

made for the removal of phenol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phenol, the person performing the operation should be informed of phenol's hazardous properties.

- Where there is any possibility of exposure of an employee's body to solid or liquid phenol or liquids containing phenol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with phenol should be removed immediately and not reworn until the phenol is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid phenol or liquids containing phenol contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid or liquid phenol or liquids containing phenol, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with phenol should be immediately washed or showered with soap or mild detergent and water to remove any phenol.
- Any clothing which becomes wet with liquid phenol or liquids containing phenol should be removed immediately and not reworn until the phenol is removed from the clothing.
- Eating and smoking should not be permitted in areas where solid or liquid phenol or liquids containing phenol are handled, processed, or stored.
- Employees who handle solid or liquid phenol or liquids containing phenol should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phenol may occur and control methods which may be effective in each case:

Operation	Controls
Application and curing of bonding resin in plywood manufacture; application and curing of molding resins in manufacture of molded articles, such as	Process enclosure; local exhaust ventilation; personal protective equipment

should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

- **Method**

Sampling and analyses may be performed by collection of phenol in a bubbler containing sodium hydroxide, followed by treatment with sulfuric acid, and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure phenol may be used. An analytical method for phenol is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

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- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with solid or liquid phenol or liquids containing phenol.
- If employees' clothing has had any possibility of being contaminated with solid or liquid phenol or liquids containing phenol, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing which has had any possibility of being contaminated with solid or liquid phenol or liquids containing phenol should be placed in closed containers for storage until it can be discarded or until provision is

made for the removal of phenol from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the phenol, the person performing the operation should be informed of phenol's hazardous properties.

- Where there is any possibility of exposure of an employee's body to solid or liquid phenol or liquids containing phenol, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with phenol should be removed immediately and not reworn until the phenol is removed from the clothing.
- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solid or liquid phenol or liquids containing phenol contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to solid or liquid phenol or liquids containing phenol, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with phenol should be immediately washed or showered with soap or mild detergent and water to remove any phenol.
- Any clothing which becomes wet with liquid phenol or liquids containing phenol should be removed immediately and not reworn until the phenol is removed from the clothing.
- Eating and smoking should not be permitted in areas where solid or liquid phenol or liquids containing phenol are handled, processed, or stored.
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COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phenol may occur and control methods which may be effective in each case:

Operation	Controls
Application and curing of bonding resin in plywood manufacture; application and curing of molding resins in manufacture of molded articles, such as	Process enclosure; local exhaust ventilation; personal protective equipment

electrical appliances, automotive parts, foundry sand molds, and utensil handles; manufacture of friction materials, bonded abrasives, coated abrasives, wood particle board, and insulation materials		Use in synthesis of intermediates in polyester production; production of corrosion-resistant polyester and polyester polyols; use in synthesis of dye intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in industrial coatings in drum and can linings, milk and beer-processing equipment, water tanks and air-conditioning equipment, decorative laminates, and textile coatings	Process enclosure; local exhaust ventilation; personal protective equipment	Use in synthesis of surface-active agents and detergent intermediates; in synthesis of explosives	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of thermosetting phenolic resins, epoxy, polycarbonate, phenoxy, and polysulfone; synthesis of aprotactam for use in nylon 6 fibers, plastics, and films	Process enclosure; local exhaust ventilation; personal protective equipment	Use in manufacture of disinfectant agents and products for industrial and household use	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of agricultural chemicals and intermediates; synthesis of pharmaceuticals, rubber and plastic plasticizers, antioxidants, curing agents, and intermediates	Process enclosure; local exhaust ventilation; personal protective equipment	Use in synthesis of synthetic cresols and xylenols	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of stabilizers and preservatives for dyes, perfumes, and fungicides	Process enclosure; local exhaust ventilation; personal protective equipment		
Use during solvent refining of lubrication oil and wax; use in synthesis of additives for gasoline and lubricating fluids and intermediates	Process enclosure; local exhaust ventilation; personal protective equipment		

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If solid or liquid phenol or liquids containing phenol get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If solid or liquid phenol or liquids containing phenol get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid phenol or liquids containing phenol penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

• Breathing

If a person breathes in large amounts of phenol, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When solid or liquid phenol or liquids containing phenol have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

electrical appliances, automotive parts, foundry sand molds, and utensil handles; manufacture of friction materials, bonded abrasives, coated abrasives, wood particle board, and insulation materials		Use in synthesis of intermediates in polyester production; production of corrosion-resistant polyester and polyester polyols; use in synthesis of dye intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in industrial coatings in drum and can linings, milk and beer-processing equipment, water tanks and air-conditioning equipment, decorative laminates, and textile coatings	Process enclosure; local exhaust ventilation; personal protective equipment	Use in synthesis of surface-active agents and detergent intermediates; in synthesis of explosives	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of thermosetting phenolic resins, epoxy, polycarbonate, phenoxy, and polysulfone; synthesis of aprotactam for use in nylon 6 fibers, plastics, and films	Process enclosure; local exhaust ventilation; personal protective equipment	Use in manufacture of disinfectant agents and products for industrial and household use	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of agricultural chemicals and intermediates; synthesis of pharmaceuticals, rubber and plastic plasticizers, antioxidants, curing agents, and intermediates	Process enclosure; local exhaust ventilation; personal protective equipment	Use in synthesis of synthetic cresols and xlenols	Process enclosure; local exhaust ventilation; personal protective equipment
Use in synthesis of stabilizers and preservatives for dyes, perfumes, and fungicides	Process enclosure; local exhaust ventilation; personal protective equipment		
Use during solvent refining of lubrication oil and wax; use in synthesis of additives for gasoline and lubricating fluids and intermediates	Process enclosure; local exhaust ventilation; personal protective equipment		

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If solid or liquid phenol or liquids containing phenol get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If solid or liquid phenol or liquids containing phenol penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

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When solid or liquid phenol or liquids containing phenol have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If phenol is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill.
2. If in the solid form, for small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber.
3. If in the liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber.

- Waste disposal methods:

Phenol may be disposed of:

1. If in the solid form, by making packages of phenol in paper or other flammable material and burning in a suitable combustion chamber, or by dissolving phenol in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.
2. If in the liquid form, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill, or by atomizing the liquid in a suitable combustion chamber.

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- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

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- If phenol is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill.
2. If in the solid form, for small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dissolve in a flammable solvent (such as alcohol) and atomize in a suitable combustion chamber.
3. If in the liquid form, for small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber.

- Waste disposal methods:

Phenol may be disposed of:

1. If in the solid form, by making packages of phenol in paper or other flammable material and burning in a suitable combustion chamber, or by dissolving phenol in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber.
2. If in the liquid form, by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill, or by atomizing the liquid in a suitable combustion chamber.

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RESPIRATORY PROTECTION FOR PHENOL

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor or Particulate Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust and mist filter(s). Any supplied-air respirator. Any self-contained breathing apparatus.
100 ppm or less	A chemical cartridge respirator with a full facepiece, organic vapor cartridge(s), and dust and mist filter(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of phenol; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 100 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

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Occupational Health Guideline for 1,1,2,2-Tetrachloroethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $\text{CHCl}_2\text{CHCl}_2$
- Synonyms: Symmetrical-tetrachloroethane; acetylene tetrachloride; sym-tetrachloroethane
- Appearance and odor: Colorless or pale yellow liquid with a sickly sweet odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2,2-tetrachloroethane is 5 parts of 1,1,2,2-tetrachloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of 1,1,2,2-tetrachloroethane per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 1 ppm ($6.87 \text{ mg}/\text{m}^3$) averaged over a 10-hour work shift. The NIOSH Criteria Document for 1,1,2,2-Tetrachloroethane should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

1,1,2,2-Tetrachloroethane can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

• Effects of overexposure

1. *Short-term Exposure:* Breathing in high concentrations of 1,1,2,2-tetrachloroethane may cause irritation of the eyes and nose, nausea, vomiting, and drowsiness. Liver and kidney damage may occur. If the exposure was severe, within a few hours a deep dusky coloration

of the skin may appear, followed by unconsciousness and death. If the exposed worker is removed immediately, he may recover completely but should be placed under observation in case late symptoms appear. If the vapor or liquid of 1,1,2,2-tetrachloroethane gets into the eyes, it may cause watering and burning. It may cause serious eye damage unless immediate medical care is obtained.

2. *Long-term Exposure:* Prolonged or repeated exposure to 1,1,2,2-tetrachloroethane, either by breathing or by absorbing it through the skin, may cause fatigue, loss of appetite, tremors, weight loss, constipation, heart damage, blood changes, kidney damage, abdominal distress or pain, vomiting, dizziness, tenderness, liver damage with such symptoms as pain over the liver, dark urine, and yellow jaundice. Reproductive abnormalities have been noted in studies of animals following exposure to high levels of 1,1,2,2-tetrachloroethane. Prolonged or repeated skin contact with 1,1,2,2-tetrachloroethane may also cause skin irritation.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1,2,2-tetrachloroethane.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to 1,1,2,2-tetrachloroethane at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver, kidneys, and central nervous system should be stressed.

—Liver function tests: 1,1,2,2-Tetrachloroethane causes liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Occupational Health Guideline for 1,1,2,2-Tetrachloroethane

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $\text{CHCl}_2\text{CHCl}_2$
- Synonyms: Symmetrical-tetrachloroethane; acetylene tetrachloride; sym-tetrachlorethane
- Appearance and odor: Colorless or pale yellow liquid with a sickly sweet odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2,2-tetrachloroethane is 5 parts of 1,1,2,2-tetrachloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of 1,1,2,2-tetrachloroethane per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be reduced to 1 ppm ($6.87 \text{ mg}/\text{m}^3$) averaged over a 10-hour work shift. The NIOSH Criteria Document for 1,1,2,2-Tetrachloroethane should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**
1,1,2,2-Tetrachloroethane can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.
- **Effects of overexposure**
 1. **Short-term Exposure:** Breathing in high concentrations of 1,1,2,2-tetrachloroethane may cause irritation of the eyes and nose, nausea, vomiting, and drowsiness. Liver and kidney damage may occur. If the exposure was severe, within a few hours a deep dusky coloration

of the skin may appear, followed by unconsciousness and death. If the exposed worker is removed immediately, he may recover completely but should be placed under observation in case late symptoms appear. If the vapor or liquid of 1,1,2,2-tetrachloroethane gets into the eyes, it may cause watering and burning. It may cause serious eye damage unless immediate medical care is obtained.

2. **Long-term Exposure:** Prolonged or repeated exposure to 1,1,2,2-tetrachloroethane, either by breathing or by absorbing it through the skin, may cause fatigue, loss of appetite, tremors, weight loss, constipation, heart damage, blood changes, kidney damage, abdominal distress or pain, vomiting, dizziness, tenderness, liver damage with such symptoms as pain over the liver, dark urine, and yellow jaundice. Reproductive abnormalities have been noted in studies of animals following exposure to high levels of 1,1,2,2-tetrachloroethane. Prolonged or repeated skin contact with 1,1,2,2-tetrachloroethane may also cause skin irritation.

3. **Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1,2,2-tetrachloroethane.

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The following medical procedures should be made available to each employee who is exposed to 1,1,2,2-tetrachloroethane at potentially hazardous levels:

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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—Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

• **Summary of toxicology**

1,1,2,2-Tetrachloroethane is highly toxic to the liver and is a central nervous system depressant. Rats exposed to 500 ppm for 4 hours survived, but 1,000 ppm was fatal. Reports of industrial experience indicate that cases of mild intoxication have presented symptoms of gastrointestinal irritation (nausea, vomiting, abdominal pain, anorexia) and central nervous system effects (dizziness, headache, irritability, nervousness, insomnia); more severe exposure resulted in liver involvement (enlarged and tender liver, jaundice, bilirubinuria), nephritis (albuminuria and casts); and tremors of hands and eyelids. In cases of severe industrial intoxication, there was hepatic necrosis with jaundice, sometimes progressing to cirrhosis; individuals who died during the acute stage also showed cerebral edema and pulmonary edema with hemorrhage, as well as liver and kidney injury. One study reported that human subjects exposed to 335 ppm for 10 minutes or 186 ppm for 30 minutes noted a disagreeable odor; there were some upper respiratory irritation and central nervous system effects. Among a group of workers in India exposed to 20-65 ppm there was nausea, vomiting, and abdominal pain and a high incidence of tremor of the hands. Prolonged skin exposure may be expected to produce dermatitis due to defatting action. Eye damage has been reported.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 167.8
2. Boiling point (760 mm Hg): 146 C (295 F)
3. Specific gravity (water = 1): 1.6
4. Vapor density (air = 1 at boiling point of 1,1,2,2-tetrachloroethane): 5.8
5. Melting point: -42.5 C (-44.5 F)
6. Vapor pressure at 20 C (68 F): 8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.29
8. Evaporation rate (butyl acetate = 1): 0.65

• **Reactivity**

1. Conditions contributing to instability: Heat: unusual exposure to light in the presence of air may form small amounts of phosgene.
2. Incompatibilities: Reacts with chemically active metals or with strong caustics. In the presence of steam, contact with hot iron, aluminum, and zinc may cause formation of toxic vapors.
3. Hazardous decomposition products: Toxic gases and vapors (such as phosgene, hydrogen chloride, chlorinated solvents, and carbon monoxide) may be

released when 1,1,2,2-tetrachloroethane decomposes.

4. Special precautions: Liquid 1,1,2,2-tetrachloroethane will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Not combustible

• **Warning properties**

Patty states that the odor of 1,1,2,2-tetrachloroethane is detectable at 5 ppm (3 ppm, according to Lehmann). Since the odor threshold is at (or below) the permissible exposure limit, this compound is treated as a material with good warning properties.

Grant indicates that this compound is not an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,1,2,2-tetrachloroethane may be used. An analytical method for 1,1,2,2-tetrachloroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

PB 265 028).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

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- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid 1,1,2,2-tetrachloroethane.
- Clothing contaminated with liquid 1,1,2,2-tetrachloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1,2,2-tetrachloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1,2,2-tetrachloroethane, the person performing the operation should be informed of 1,1,2,2-tetrachloroethane's hazardous properties.
- Where exposure of an employee's body to liquid 1,1,2,2-tetrachloroethane may occur, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with liquid 1,1,2,2-tetrachloroethane should be removed immediately and not reworn until the 1,1,2,2-tetrachloroethane is removed from the clothing.
- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid 1,1,2,2-tetrachloroethane contacting the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid 1,1,2,2-tetrachloroethane, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes contaminated with liquid 1,1,2,2-tetrachloroethane should be immediately washed or showered with soap or mild detergent and water to remove any 1,1,2,2-tetrachloroethane.
- Eating and smoking should not be permitted in areas where liquid 1,1,2,2-tetrachloroethane is handled, processed, or stored.
- Employees who handle liquid 1,1,2,2-tetrachloroethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1,2,2-tetrachloroethane may occur and control methods which may be effective in each case:

Operation

Controls

Use as a chemical intermediate in manufacture of tetrachloroethylene and trichloroethylene; use in cleaning and extraction processes; use in chlorination of phthalic anhydride; use in manufacture of cyanogen chloride, polymers, and tetrachloro-alkylphenol	Local exhaust ventilation; general dilution ventilation
Use as a fumigant in greenhouses	Personal protective equipment
Use in manufacture of lacquers and varnishes, paint and varnish removers	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation during use and preparation of insecticides and weed killers	Local exhaust ventilation; general dilution ventilation; personal protective equipment
Use in cleaning and degreasing of metals	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a solvent in preparation of adhesives	Local exhaust ventilation
Use during addition to aliphatic alcohols and acetates to improve solvency for nitrocellulose and cellulose acetate as in photographic film	Local exhaust ventilation
Use in application of adhesives	General dilution ventilation; personal protective equipment
Use in refining of waxes and resins	Local exhaust ventilation

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If 1,1,2,2-tetrachloroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical

- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid 1,1,2,2-tetrachloroethane.
- Clothing contaminated with liquid 1,1,2,2-tetrachloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1,2,2-tetrachloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1,2,2-tetrachloroethane, the person performing the operation should be informed of 1,1,2,2-tetrachloroethane's hazardous properties.
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- Non-impervious clothing which becomes contaminated with liquid 1,1,2,2-tetrachloroethane should be removed immediately and not reworn until the 1,1,2,2-tetrachloroethane is removed from the clothing.
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- Skin that becomes contaminated with liquid 1,1,2,2-tetrachloroethane should be immediately washed or showered with soap or mild detergent and water to remove any 1,1,2,2-tetrachloroethane.
- Eating and smoking should not be permitted in areas where liquid 1,1,2,2-tetrachloroethane is handled, processed, or stored.
- Employees who handle liquid 1,1,2,2-tetrachloroethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1,2,2-tetrachloroethane may occur and control methods which may be effective in each case:

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Use as a chemical intermediate in manufacture of tetrachloroethylene and trichloroethylene; use in cleaning and extraction processes; use in chlorination of phthalic anhydride; use in manufacture of cyanogen chloride, polymers, and tetrachloro-alkylphenol	Local exhaust ventilation; general dilution ventilation
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Use in refining of waxes and resins	Local exhaust ventilation

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In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If 1,1,2,2-tetrachloroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical

attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If 1,1,2,2-tetrachloroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2,2-tetrachloroethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of 1,1,2,2-tetrachloroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When 1,1,2,2-tetrachloroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If 1,1,2,2-tetrachloroethane is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- **Waste disposal method:**

1,1,2,2-Tetrachloroethane may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

ADDITIONAL INFORMATION

To find additional information on 1,1,2,2-tetrachloroethane, look up 1,1,2,2-tetrachloroethane in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for 1,1,2,2-Tetrachloroethane (December 1976)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for 1,1,2,2-Tetrachloroethane (December 1976)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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RESPIRATORY PROTECTION FOR 1,1,2,2-TETRACHLOROETHANE

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Vapor Concentration	
50 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
150 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 150 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for Tetrachloroethylene*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $\text{CCl}_2 = \text{CCl}_2$
- Synonyms: Perchloroethylene; perchlorethylene; tetrachlorethylene; perk
- Appearance and odor: Colorless liquid with an odor like chloroform or ether.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for tetrachloroethylene is 100 parts of tetrachloroethylene per million parts of air (ppm) averaged over an eight-hour work shift, with a ceiling level of 200 ppm and a maximum acceptable peak of 300 ppm for 5 minutes in any three-hour period. NIOSH has recommended that the permissible exposure limit be reduced to 50 ppm (339 mg/m³) averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 100 ppm (678 mg/m³) averaged over a 15-minute period. The NIOSH Criteria Document for Tetrachloroethylene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Tetrachloroethylene can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

• Effects of overexposure

1. *Short-term Exposure:* Tetrachloroethylene may cause headache, nausea, drowsiness, dizziness, incoordination, and unconsciousness. It may also cause irritation of

the eyes, nose, and throat and flushing of the face and neck. In addition, it might cause liver damage with such findings as yellow jaundice and dark urine. The liver damage may become evident several weeks after the exposure.

2. *Long-term Exposure:* Prolonged or repeated overexposure to liquid tetrachloroethylene may cause irritation of the skin. It might also cause damage to the liver and kidneys.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to tetrachloroethylene.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to tetrachloroethylene at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and the cardiovascular and neurological systems should be stressed. The skin should be examined for evidence of chronic disorders.

—Liver function tests: Tetrachloroethylene may cause liver damage. A profile of liver function should be obtained by using a medically acceptable array of biochemical tests.

—Urinalysis: Since kidney damage has also been observed from exposure, a urinalysis should be obtained to include at minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis.

• Summary of toxicology

Tetrachloroethylene vapor is a narcotic. Rats did not survive when exposed for longer than 12-18 minutes to 12,000 ppm; when exposed repeatedly to 470 ppm they showed liver and kidney injury. Cardiac arrhythmias

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
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CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 165.85
2. Boiling point (760 mm Hg): 121.2 C (250 F)
3. Specific gravity (water = 1): 1.62
4. Vapor density (air = 1 at boiling point of tetrachloroethylene): 5.83
5. Melting point: -22.4 C (-8 F)
6. Vapor pressure at 20 C (68 F): 14 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.015
8. Evaporation rate (butyl acetate = 1): 2.8

• Reactivity

1. Conditions contributing to instability: Heat.
2. Incompatibilities: Tetrachloroethylene reacts with strong oxidizers and chemically active metals such as barium, lithium, and beryllium.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released when tetrachloroethylene decomposes.

oethylene decomposes.

4. Special precautions: Liquid tetrachloroethylene will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Not combustible

• Warning properties

1. Odor Threshold: Both May and Stern state that 50 ppm is the odor threshold for tetrachloroethylene.

2. Eye Irritation Level: Grant reports that "exposure to high concentrations of (tetrachloroethylene) vapor causes mild sensation of irritation to the eyes, but serious injury is not likely." The exact concentrations producing irritation are not mentioned by Grant.

Spector, however, reports that after a 20- to 30-minute exposure to 206 to 235 ppm, eye irritation occurs in humans.

Patty reports "very slight irritation of the eyes" among humans at 106 ppm.

3. Other Information: Spector reports that a 10-minute exposure to 513 to 690 ppm produces nose and throat irritation.

4. Evaluation of Warning Properties: Since the odor threshold of tetrachloroethylene is below the permissible exposure limit, and since eye irritation occurs at a concentration only twice the permissible exposure limit, its warning properties are considered to be adequate.

MONITORING AND MEASUREMENT PROCEDURES

• Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of tetrachloroethylene. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Peak Above Ceiling Evaluation

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of tetrachloroethylene. Each measurement should consist of a 30-minute sample or a series of consecutive samples totalling 30 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of

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three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure tetrachloroethylene may be used. An analytical method for tetrachloroethylene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid tetrachloroethylene.
- Non-impervious clothing which becomes contaminated with liquid tetrachloroethylene should be removed promptly and not reworn until the tetrachloroethylene is removed from the clothing.
- Clothing wet with liquid tetrachloroethylene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of tetrachloroethylene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the tetrachloroethylene, the person performing the operation should be informed of tetrachloroethylene's hazardous properties.

- Employees should be provided with and required to use splash-proof safety goggles where liquid tetrachloroethylene may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid tetrachloroethylene should be promptly washed or showered with soap or mild detergent and water to remove any tetrachloroethylene.
- Employees who handle liquid tetrachloroethylene should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to tetrachloroethylene may occur and control methods which may be effective in each case:

Operation	Controls
Use as dry cleaning solvent; as degreasing and metal cleaning agent; in vapor degreasing of metal parts	Local exhaust ventilation; general dilution; personal protective equipment
Use as chemical intermediate in production of fluorocarbons, pesticides, and trichloroacetic acid	Process enclosure; local exhaust ventilation; general dilution ventilation
Use as scouring, sizing, desizing, solvent and greaser remover in processing and finishing of textiles	Local exhaust ventilation; general dilution; personal protective equipment
Use as general industrial solvent in rubber, textile, printing, soap, and paint remover industries	Local exhaust ventilation; general dilution; personal protective equipment
Use as extraction agent for vegetable and mineral oils and in pharmaceutical industry; as vermifuge; as laundry treatment for presoaking and as drying medium in metal and wood industries	Local exhaust ventilation; general dilution ventilation; personal protective equipment

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EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If tetrachloroethylene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If tetrachloroethylene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If tetrachloroethylene soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of tetrachloroethylene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When tetrachloroethylene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If tetrachloroethylene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

- **Waste disposal method:**

Tetrachloroethylene may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

REFERENCES

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EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If tetrachloroethylene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If tetrachloroethylene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If tetrachloroethylene soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of tetrachloroethylene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When tetrachloroethylene has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If tetrachloroethylene is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect for reclamation or absorb in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Tetrachloroethylene may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

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* SPECIAL NOTE

Tetrachloroethylene appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980). The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 20, 1979.

RESPIRATORY PROTECTION FOR TETRACHLOROETHYLENE

Condition	Minimum Respiratory Protection* Required Above 100 ppm
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s). A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.
*Only NIOSH-approved or MSHA-approved equipment should be used.	

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Occupational Health Guideline for Toluene

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $C_6H_5CH_3$
- Synonyms: Toluol; phenylmethane; methylbenzene
- Appearance and odor: Colorless liquid with an aromatic odor, like benzene.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for toluene is 200 parts of toluene per million parts of air (ppm) averaged over an eight-hour work shift, and during any such work shift, 300 ppm toluene may not be exceeded except that a peak of 500 ppm toluene is permitted for 10 minutes during the eight-hour work shift. NIOSH has recommended that the permissible exposure limit be reduced to 100 ppm toluene averaged over an eight-hour work shift with a ceiling level of 200 ppm averaged over a ten-minute period. The NIOSH Criteria Document for Toluene should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

• Routes of exposure

Toluene can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

• Effects of overexposure

1. **Short-term Exposure:** Toluene may cause irritation of the eyes, respiratory tract, and skin. It may also cause fatigue, weakness, confusion, headache, dizziness, and drowsiness. Peculiar skin sensation may be produced

such as a "pins and needles feeling" or numbness. Very high concentrations may cause unconsciousness and death. The liquid splashed in the eye may cause irritation and temporary damage. Inhalation may also cause difficulty in seeing in bright light. If liquid toluene is splashed in the eyes, it will cause temporary irritation.

2. **Long-term Exposure:** Repeated or prolonged exposure to liquid toluene may cause drying and cracking of the skin.

3. **Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to toluene.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to toluene at potentially hazardous levels:

1. **Initial Medical Examination:**

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the central nervous system, liver and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since proper kidney function is necessary for biologic monitoring, a urinalysis should be obtained to include at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. The urine should be analyzed for hippuric acid to obtain a background level.

2. **Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis. Hippuric acid level in urine may be an indicator of the level of toluene exposure.

• Summary of toxicology

Toluene vapor causes narcosis. Controlled exposure of human subjects to 200 ppm for 8 hours produced mild fatigue, weakness, confusion, lacrimation, and paresthesia; at 600 ppm for 8 hours there were also euphoria, headache, dizziness, dilated pupils and nausea; at 800

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Public Health Service Centers for Disease Control
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- ppm for 8 hours, symptoms were more pronounced, and after-effects included nervousness, muscular fatigue, and insomnia persisting for several days. Severe but reversible liver and kidney injury occurred in a person who was a glue-sniffer for 3 years; the chief component of the inhaled solvent was toluene (80% V/V); other ingredients were not listed. In workers exposed for many years to concentrations in the range of 80 to 300 ppm, there was no clinical or laboratory evidence of altered liver function. Toluene exposure does not result in the hematopoietic effects caused by benzene; the myelotoxic effects previously attributed to toluene are judged by more recent investigations to be the result of concurrent exposure to benzene present as a contaminant in the commercial toluene used. Most of the toluene absorbed from inhalation is metabolized to benzoic acid, conjugated with glycine in the liver to form hippuric acid, and excreted in the urine; the average amount of hippuric acid excreted in the urine by individuals not exposed to toluene is approximately 0.7 to 1.0 g/l of urine. The liquid splashed in the eyes of two workers caused transient corneal damage and conjunctival irritation; complete recovery occurred within 48 hours. Repeated or prolonged skin contact with liquid toluene has a defatting action, causing drying, fissuring, and dermatitis.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 92.1
2. Boiling point (760 mm Hg): 111 C (231 F)
3. Specific gravity (water = 1): 0.86
4. Vapor density (air = 1 at boiling point of toluene): 3.14
5. Melting point: -95 C (-139 F)
6. Vapor pressure at 20 C (68 F): 22 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.05
8. Evaporation rate (butyl acetate = 1): 2.24

• Reactivity

1. Conditions contributing to instability: Containers may burst at elevated temperatures.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon dioxide and carbon monoxide) may be released in a fire involving toluene.
4. Special precautions: Toluene will attack some forms of plastics, rubber, and coatings.

• Flammability

1. Flash point: 4 C (40 F) (closed cup)
2. Autoignition temperature: 480 C (896 F)
3. Flammable limits in air, % by volume: Lower: 1.27; Upper: 7.1
4. Extinguishant: Carbon dioxide, dry chemical, foam

• Warning properties

1. Odor Threshold: The American National Stand-

ards Institute (ANSI) states that "the odor of toluene is detectable by most people at concentrations in the range of 10 to 15 ppm. The odor has little value as a warning property."

Patty points out that olfactory fatigue occurs rapidly upon exposure to toluene.

2. Eye Irritation Level: Grant states that "the vapors of toluene cause noticeable sensation of irritation to human eyes at 300 to 400 ppm in air, but even at 800 ppm irritation is slight."

ANSI reports that "irritation of eyes, mucous membranes, and upper respiratory tract may occur while workers are exposed to low concentrations of toluene. There is a considerable range of variation (100 to 500 ppm) between individuals, some finding any concentration of toluene objectionable. Commercial grades of toluene vary in irritant properties."

3. Evaluation of Warning Properties: Because of its irritant effects, toluene is judged to have good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of toluene. Each measurement should consist of a ten (10) minute sample or series of consecutive samples totalling ten (10) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• Peak Above Ceiling Evaluation

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• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent desorption of toluene with carbon disulfide and gas

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• Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent desorption of toluene with carbon disulfide and gas

chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure toluene may be used. An analytical method for toluene is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

Methods for Set V" (order number PB 262 524).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid toluene.
- Any clothing which becomes wet with liquid toluene should be removed immediately and not reworn until the toluene is removed from the clothing.
- Clothing wet with toluene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of toluene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the toluene, the person performing the operation should be informed of toluene's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid toluene may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to toluene, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid toluene should be promptly washed or showered with soap or mild detergent and water to remove any toluene.
- Employees who handle liquid toluene should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to toluene may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in pharmaceutical, chemical, rubber, and plastics industries; as a thinner for paints, lacquer, coatings, and dyes; as a paint remover; insecticides	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as starting material and intermediate in organic chemical and chemical synthesis industries	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of artificial leather; fabric and paper coatings; photogravure ink production; spray surface coating; as a diluent (cellulose ester lacquers)	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as constituent in formulation of automotive and aviation fuels	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment

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In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If liquid toluene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

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If liquid toluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and

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- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid toluene.
- Any clothing which becomes wet with liquid toluene should be removed immediately and not reworn until the toluene is removed from the clothing.
- Clothing wet with toluene should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of toluene from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the toluene, the person performing the operation should be informed of toluene's hazardous properties.
- Employees should be provided with and required to use splash-proof safety goggles where liquid toluene may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to toluene, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

- Skin that becomes wet with liquid toluene should be promptly washed or showered with soap or mild detergent and water to remove any toluene.
- Employees who handle liquid toluene should wash their hands thoroughly with soap or mild detergent and water before eating or smoking.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to toluene may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent in pharmaceutical, chemical, rubber, and plastics industries; as a thinner for paints, lacquer, coatings, and dyes; as a paint remover; insecticides	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as starting material and intermediate in organic chemical and chemical synthesis industries	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use in manufacture of artificial leather; fabric and paper coatings; photogravure ink production; spray surface coating; as a diluent (cellulose ester lacquers)	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment
Use as constituent in formulation of automotive and aviation fuels	Process enclosure; general dilution ventilation; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If liquid toluene gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If liquid toluene gets on the skin, promptly wash the contaminated skin using soap or mild detergent and

water. If liquid toluene soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

- **Breathing**

If a person breathes in large amounts of toluene, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

- **Swallowing**

When toluene has been swallowed, get medical attention immediately. Do not attempt to make the exposed person vomit.

- **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If toluene is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be reclaimed or collected and atomized in a suitable combustion chamber. Toluene should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion. Sewers designed to preclude the formation of explosive concentrations of toluene vapors are permitted.

- **Waste disposal method:**

Toluene may be disposed of by atomizing in a suitable combustion chamber.

ADDITIONAL INFORMATION

To find additional information on toluene, look up toluene in the following documents:

- Medical Surveillance for Chemical Hazards
- Respiratory Protection for Chemical Hazards
- Personal Protection and Sanitation for Chemical Hazards
- NIOSH Criteria Document for Toluene (July 1973)

These documents are available through the NIOSH Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "Toluene," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
- American Industrial Hygiene Association: "Toluene," *Hygienic Guide Series*, Detroit, Michigan, 1957.
- American National Standard Acceptable Concentrations - Toluene: ANSI-Z37.12-1974, American National Standards Institute, Inc., New York, 1974.
- American Petroleum Institute: "Toluene," *API Toxicological Reviews*, New York, 1960.
- Christensen, H. E., and Luginbyhl, T. L. (eds.): *NIOSH Toxic Substances List*, 1974 Edition, HEW Publication No. 74-134, 1974.
- Dow Chemical Company: *Material Safety Data Sheet - Toluene*, Midland, Michigan, 1972.
- Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
- International Labour Office: *Encyclopedia of Occupational Health and Safety*, McGraw-Hill, New York, 1971.
- National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: *Criteria for a Recommended Standard Occupational Exposure to Toluene*, HEW Publication No. HSM 73-11023, GPO No. 017-033-00019, U.S. Government Printing Office, Washington, D.C., 1973.
- "Occupational Exposure to Toluene," *Federal Register*, 40:46206-46219, October 6, 1975.
- Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
- Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
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RESPIRATORY PROTECTION FOR TOLUENE

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapor Concentration	
500 ppm or less	Any chemical cartridge respirator with an organic vapor cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
1000 ppm or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s).
2000 ppm or less	A gas mask with a chin-style or a front- or back-mounted organic vapor canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

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Occupational Health Guideline for 1,1,2-Trichloroethane *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $\text{CHCl}_2\text{CH}_2\text{Cl}$
- Synonyms: Vinyl trichloride; beta-trichloroethane
- Appearance and odor: Colorless liquid with a sweet odor, like chloroform.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 1,1,2-trichloroethane is 10 parts of 1,1,2-trichloroethane per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 45 milligrams of 1,1,2-trichloroethane per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

• Routes of exposure

1,1,2-Trichloroethane can affect the body if it is inhaled if it comes in contact with the eyes or skin, or if it is swallowed. It may be absorbed through the skin.

• Effects of overexposure

1. **Short-term Exposure:** 1,1,2-Trichloroethane may cause irritation of the eyes and nose, drowsiness, incoordination, unconsciousness, and death. It might also cause liver and kidney damage.

2. **Long-term Exposure:** Repeated or prolonged exposure to 1,1,2-trichloroethane might cause liver or kidney damage.

3. **Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 1,1,2-trichloroethane.

• Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to 1,1,2-trichloroethane at potentially hazardous levels:

1. **Initial Medical Screening:** Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 1,1,2-trichloroethane exposure.

—Liver disease: 1,1,2-Trichloroethane causes liver damage in animals and justifies consideration before exposing persons with impaired liver function.

—Kidney disease: 1,1,2-Trichloroethane causes kidney damage in animals and justifies special consideration in those with impaired renal function.

2. **Periodic Medical Examination:** Any employee developing the above-listed conditions should be referred for further medical examination.

• Summary of toxicology

1,1,2-Trichloroethane vapor is a potent narcotic. Injury to lungs, liver, and kidneys has been observed in animals. The lethal concentration for rats was 2000 ppm for 4 hours. Concentrations resulting in narcosis also caused irritation of the nose and eyes. Mice treated by intraperitoneal injection with anesthetic doses showed moderate hepatic dysfunction and renal dysfunction; at autopsy, there was centrilobular necrosis of the liver and tubular necrosis of the kidney. No human cases of intoxication or systemic effects from industrial exposure have been reported.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data

1. Molecular weight: 133.4
2. Boiling point (760 mm Hg): 113 C (236 F)
3. Specific gravity (water = 1): 1.43
4. Vapor density (air = 1 at boiling point of 1,1,2-trichloroethane): 4.55
5. Melting point: -37 C (-34 F)
6. Vapor pressure at 20 C (68 F): 18.8 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F):

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Occupational Health Guideline for 1,1,2-Trichloroethane *

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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES

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U.S. DEPARTMENT OF LABOR

Occupational Safety and Health Administration

0.45

8. Evaporation rate (butyl acetate = 1): Data not available

- **Reactivity**

1. Conditions contributing to instability: Heat.

2. Incompatibilities: Contact with strong oxidizers, strong caustics, and chemically active metals such as aluminum and magnesium powders, sodium or potassium may cause fires and explosions.

3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride, phosgene, and carbon monoxide) may be released in a fire involving 1,1,2-trichloroethane.

4. Special precautions: Liquid 1,1,2-trichloroethane will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: None in normal test method

2. Autoignition temperature: Data not available

3. Flammable limits in air, % by volume: Lower: 6.0; Upper: 15.5 (high energy ignition source required)

4. Extinguishant: Foam, carbon dioxide, dry chemical

- **Warning properties**

1. Odor Threshold: Although 1,1,2-trichloroethane is known to have a sweet, chloroform-like odor, no quantitative data are available concerning the odor threshold of this substance.

2. Eye Irritation Level: Grant reports that high concentrations of the vapors are irritating to the eyes. The concentrations at which this irritation occurs are not stated.

3. Other Information: Grant reports that high concentrations of the vapors are irritating to the respiratory tract, but no quantitative information is given.

4. Evaluation of Warning Properties: Since no quantitative information is available relating the warning properties to air concentrations of 1,1,2-trichloroethane, this substance has been treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of vapors using an adsorption tube with subsequent desorption with carbon disulfide and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure 1,1,2-trichloroethane may be

used. An analytical method for 1,1,2-trichloroethane is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

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- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid 1,1,2-trichloroethane.

- Clothing wet with liquid 1,1,2-trichloroethane should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 1,1,2-trichloroethane from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 1,1,2-trichloroethane, the person performing the operation should be informed of 1,1,2-trichloroethane's hazardous properties.

- Non-impervious clothing which becomes contaminated with liquid 1,1,2-trichloroethane should be removed promptly and not reworn until the 1,1,2-trichloroethane is removed from the clothing.

- Employees should be provided with and required to use splash-proof safety goggles where liquid 1,1,2-trichloroethane may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid 1,1,2-trichloroethane should be promptly washed or showered with soap or mild detergent and water to remove any 1,1,2-trichloroethane.

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- Employees should be provided with and required to use splash-proof safety goggles where liquid 1,1,2-trichloroethane may contact the eyes.

SANITATION

- Skin that becomes contaminated with liquid 1,1,2-trichloroethane should be promptly washed or showered with soap or mild detergent and water to remove any 1,1,2-trichloroethane.

- Eating and smoking should not be permitted in areas where liquid 1,1,2-trichloroethane is handled, processed, or stored.
- Employees who handle liquid 1,1,2-trichloroethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1,2-trichloroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use in organic synthesis in production of vinylidene chloride	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If 1,1,2-trichloroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If 1,1,2-trichloroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2-trichloroethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• Breathing

If a person breathes in large amounts of 1,1,2-trichloroethane, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing

When 1,1,2-trichloroethane has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and

know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.
- If 1,1,2-trichloroethane is spilled or leaked, the following steps should be taken:
 1. Remove all ignition sources.
 2. Ventilate area of spill or leak.
 3. Collect for reclamation or absorb in vermiculite, dry sand, or a similar material.
- Waste disposal method:

1,1,2-Trichloroethane may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

REFERENCES

- American Conference of Governmental Industrial Hygienists: "1,1,2-Trichloroethane," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Union Carbide Corporation, Industrial Medicine and Toxicology Department: *Toxicology Studies - 1,1,2-Trichloroethane*, New York, 1972.

* SPECIAL NOTE

1,1,2-Trichloroethane appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980).

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 20, 1979.

- Eating and smoking should not be permitted in areas where liquid 1,1,2-trichloroethane is handled, processed, or stored.
- Employees who handle liquid 1,1,2-trichloroethane should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 1,1,2-trichloroethane may occur and control methods which may be effective in each case:

Operation	Controls
Use in organic synthesis in production of vinylidene chloride	General dilution ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If 1,1,2-trichloroethane gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If 1,1,2-trichloroethane gets on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 1,1,2-trichloroethane soaks through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

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 2. Ventilate area of spill or leak.
 3. Collect for reclamation or absorb in vermiculite, dry sand, or a similar material.
- Waste disposal method: 1,1,2-Trichloroethane may be disposed of by absorbing it in vermiculite, dry sand, earth or a similar material and disposing in a secured sanitary landfill.

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RESPIRATORY PROTECTION FOR 1,1,2-TRICHLOROETHANE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 500 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

RESPIRATORY PROTECTION FOR 1,1,2-TRICHLOROETHANE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Vapor Concentration	
500 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
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Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
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